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The Chemical Society, founded in 1841 and first granted a Royal Charter in 1848, now numbers some 4,000 Fellows. Each Fellow is entitled to receive one copy of the Journal and of such other publications of the Society as the Council may determine, to use the Library, either directly or through the post, and to take part in the meetings of the Society. Experimental work is assisted by grants from the Research Fund. Fellows are also allowed certain privileges by kindred societies.

The publications include the *Journal*, containing papers communicated to the Society, the *Abstracts*, covering the current literature in pure Chemistry, the *Indexes*, and the *Annual Reports* on the progress of Chemistry.

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The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

with the material and industrial development of Australia. The high esteem in which Smith was held among Australasian men of science is evidenced by his election to such offices as the Presidentships of the Royal Society of New South Wales (1913), the New South Wales branch of the Australian Chemical Institute (1922—1923), and the chemistry section of the Australasian Association for the Advancement of Science. In the last-named capacity he delivered his presidential address on the chemistry of the Australian flora at Wellington, New Zealand, in 1923. He was also an original member of the Australian National Research Council, and he conducted a good deal of valuable work under the auspices of the Commonwealth Institute of Science and Industry.

Smith died at Roseville, Sydney, on September 19th, 1924, at the age of seventy-two. He was twice married, and left a widow and family, including three sons. In all the relations of life quietly genial and considerate, Smith was distinguished by his modesty and sincerity. One of the most selfless of men, he achieved without seeking it a world-wide reputation; but his reward lay in his work and in his sure knowledge of the part it was destined to play in the economic development of his adopted and beloved land of Australia. Even after passing the three score years and ten, his natural ardour and activity for chemical investigation remained in full measure. To those of the younger generation of Australian chemists who were so fortunate as to be associated with him, his unfailing enthusiasm will act as a lasting inspiration. His practical knowledge of Australian natural products was profound. In the laboratory, his diagnosis of the chemical composition of an essential oil after a few rapid superficial tests was a revelation; in the bush, the tall trees were to him as familiar friends, and his intimate knowledge of their characteristics seemed at times to border upon wizardry. In spite of initial disabilities, including lack of preliminary training, and more lasting handicaps, such as complete isolation from any centre of organic chemical activity, and with less than could have been desired in the way of encouragement and material recompense, Smith devoted well over thirty years of incessant research to the elucidation of the chemical and economic significance of these products. To the last, he was an ardent, tireless worker, who regarded every hour in the spirit of the true man of science as a potential "bringer of new things"; to the last, he remained strong in will to bring the secrets of Nature into the service of man. His pioneering work is not only of high scientific and economic worth: it will remain to him a unique and enduring monument in the annals of Australian science.

JOHN READ.

CXXVIII.—*Nitro- and Amino-ethoxylutidine.*

By John Norman Collie and Gerald Bishop.

Previous work on the nitro- and amino-lutidines (J., 1898, **73**, 229, 235) has been continued.

The ethoxylutidine (4-ethoxy-2 : 6-dimethylpyridine), b. p. 208°, was obtained from dimethylpyrone by treating it successively with ammonia, phosphorus pentachloride, and sodium ethoxide.

The *mononitroethoxylutidine* was prepared by dissolving the ethoxylutidine in strong sulphuric acid and adding a mixture of fuming nitric acid and sulphuric acid, the whole cooled in ice. After some time the mixture was poured into water, and neutralised with sodium carbonate. A bulky, white precipitate separated, m. p. 99°. The compound is slightly volatile with steam; it gives no colour with sodium hydroxide (Found: C = 54·8; H = 6·3; N = 14·5. $C_9H_{12}O_3N_2$ requires C = 55·1; H = 6·1; N = 14·3%).

Monoaminoethoxylutidine was prepared by reducing the nitro-compound with tin and hydrochloric acid. After the reaction a double tin salt crystallised out. It gave a light yellow precipitate with hydrogen sulphide [Found: Sn = 20·2; Cl = 34·9; H_2O = 1·5. $(C_9H_{14}ON_2,HCl)_3,2SnCl_4,H_2O$ requires Sn = 20·7; Cl = 34·1; H_2O = 1·5%].

The tin salt was treated with hydrogen sulphide, the filtrate evaporated to dryness, and extracted with ether. The platinum salt of the base comes down slowly, and once precipitated is very insoluble even in boiling water, or alcohol (Found: Pt = 35·9; Cl = 32·5; C = 20·0. $C_9H_{14}ON_2,HCl,PtCl_4$ requires Pt = 36·1; Cl = 32·8; C = 20·0%).

The above ethereal solution of the hydrochloride was made alkaline with sodium carbonate, and a small quantity of ammonia was evolved on evaporation. The concentrated solution was extracted with ether. On evaporation of the ethereal extract, an oil was obtained that slowly crystallised. The oil was soluble in cold water, but a concentrated solution became cloudy on warming, owing to separation of the base. The base, m. p. 62°, b. p. 267°, absorbs carbon dioxide, and is strongly alkaline. It gives a crystalline precipitate with silver nitrate, a white one with mercuric chloride, but none with lead acetate, and no colour with ferric chloride (Found: Ag = 28·0; H_2O = 8·7. $C_9H_{14}ON_2,AgNO_3,2H_2O$ requires Ag = 28·9; H_2O = 9·6%).

Oxidation of Mononitroethoxylutidine.—This compound was oxidised with a 1% solution of potassium permanganate. An acid was obtained that was easily recrystallised from hot water; m. p.

147° (Found : N = 12·5. $C_9H_{10}O_5N_2$ requires N = 12·4%). The *silver* salt is anhydrous (Found : Ag = 32·5; C = 32·5; H = 3·4. $C_9H_9O_5N_2Ag$ requires Ag = 32·4; C = 32·4; H = 2·8%), and explodes faintly on heating. The sodium and ammonium salts are easily recrystallised from water. The copper, silver, mercury, iron, and calcium salts are insoluble in water.

Oxidation of Ethoxylutidine.—This compound was oxidised with a boiling 1% solution of potassium permanganate, containing enough permanganate to oxidise one only of the methyl groups. Some ethoxylutidine remained unoxidised. The resulting acid would only crystallise when the aqueous solution was evaporated to a syrup. It could not be purified sufficiently to give a satisfactory analysis and melted unsatisfactorily at 138°. The platinum salt was therefore made [Found : Pt = 28·4. $(C_9H_{11}O_3N,HCl)_2PtCl_4$ requires Pt = 23·9%]. The *silver* salt was precipitated (Found : Ag = 38·3. $C_9H_{10}O_3NAg$ requires Ag = 37·4%).

The syrupy impure acid was heated with fuming hydriodic acid, colourless crystals, m. p. 295°, being obtained (Found : C = 48·8; H = 5·5; H_2O = 8·8. $C_7H_7O_3N,H_2O$ requires C = 49·1; H = 5·3; H_2O = 10·5%). The substance is therefore 4-hydroxy-2-methylpyridine-6-carboxylic acid.

The syrupy acid heated alone gave carbon dioxide and an ethoxypicoline, b. p. about 220°. The dried platinum salt, m. p. 207°, was analysed [Found : Pt = 28·4. $(C_8H_{11}ON,HCl)_2PtCl_4$ requires Pt = 28·5%].

The acid on further oxidation with permanganate was entirely decomposed. Nitric acid on boiling and then evaporating gave a crystalline *nitrate*, m. p. 125°, which gave the ordinary tests for a nitrate (Found : N = 11·4. $C_9H_{11}O_3N,HNO_3$ requires N = 11·5%). When the ethoxylutidine was oxidised with a slight excess of potassium permanganate over that required to oxidise both methyl groups, the product contained a mixture of the mono- and di-basic acids. An acid, m. p. 200°, was finally separated (Found : C = 51·5; H = 4·8; *M*, by titration with *N*/10-sodium hydroxide, = 210. $C_9H_9O_5N$ requires C = 51·2; H = 4·3%; *M* = 211). *Silver* salt (Found : Ag = 50·6. $C_9H_7O_5NAg_2$ requires Ag = 50·8%). *Platinum* salt (Found : Pt = 23·6. Theory requires Pt = 23·4%).

The syrupy residue from which the acid, m. p. 200°, had been separated gave carbon dioxide when heated, and on distillation a fraction, b. p. 350—360°, was obtained that solidified on cooling. It was made into the platinum salt [Found : Pt = 30·2; H_2O = 2·4. $(C_6H_7ON,HCl)_2PtCl_4,H_2O$ requires Pt = 30·2; H_2O = 2·8%]. The substance is therefore 4-hydroxy-2-methylpyridine, and has been formed by the ethyl group being oxidised by the permanganate.

The acid, m. p. 200°, when distilled, gave carbon dioxide and an oil, b. p. 200—202°. Its platinum salt melted at 215° [Found: Pt = 28·9; H_2O = 2·5. $(C_7H_9ON,HCl)_2PtCl_4$ requires Pt = 28·9; H_2O = 2·6%]. The compound therefore is 4-ethoxypyridine.

THE RALPH FORSTER LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, February 19th*, 1925.]

CXXIX.—*Reactions of Triethylphosphine.*

By JOHN NORMAN COLLIE.

THE triethylphosphine was made by Hofmann's method of adding phosphorus trichloride to an ethereal solution of zinc ethyl. After adding the sodium hydroxide and distilling off the triethylphosphine, more solid sodium hydroxide was added; an oil separated which, on boiling, dissolved with evolution of hydrogen. The residue was made acid with hydrochloric acid, evaporated to dryness, and extracted with alcohol. From the alcoholic extract diethylphosphinic acid was obtained. $PCl_3 + ZnEt_2 = ZnCl_2 + PEt_2Cl \longrightarrow PEt_2{\cdot}OH \longrightarrow PEt_2O{\cdot}OH$. This acid boiled at about 320° without decomposition. It solidified in a freezing mixture to a mass of long needles radiating from a centre. Boiled with silver hydroxide, it gave a soluble silver salt which was stable and not decomposed by boiling. After evaporation, the concentrated solution was precipitated with alcohol, the silver salt coming down in long, anhydrous, silky needles (Found: Ag = 46·6, 46·1. Calc. for $C_4H_{10}O_2PAg$, Ag = 47·0 %).

The reaction of triethylphosphine with chlorides of the non-metals is quite anomalous. If added to either phosphorus trichloride or phosphorus oxychloride, it reacts with great violence with the formation of free phosphorus. If the oxychloride be dissolved in dry ether, triethylphosphine gives a white precipitate, but this compound soon decomposes, yielding yellow phosphorus. Silicon tetrachloride and sulphur monochloride react in an exactly similar manner, silicon and sulphur being produced. It is curious that metallic chlorides do not behave in the same way. Tin tetrachloride does not react at all violently and gives a white double salt. Zinc chloride behaves also in the same manner; whilst some halogen derivatives of hydrocarbons will not react at all. Chloro- and bromobenzene may be boiled with triethylphosphine, or left for weeks with it without any reaction. Iodobenzene reacts very slowly, and four-sided plates are produced [Found: I = 39·8. $P(C_2H_5)_3(C_6H_5I)$ requires I = 39·4 %]. Trimethylene dibromide also reacts very

slowly, small, white crystals being deposited [Found : Br = 24·8. $P(C_2H_5)_3(CH_2)_3Br_2$ requires for one bromine atom, Br = 25·0 %].

Aldehydes also react with triethylphosphine. With chloral there is a powerful reaction, the chief product being metachloral, in fact if a trace only of triethylphosphine be added to chloral, after a short time the whole becomes nearly solid. When triethylphosphine is added to a solution of chloral hydrate in dry ether, an oil separates which is soluble in water and gives a chloroplatinate (Found : Pt = 21·3. $[P(C_2H_5)_3C_2H_3Cl_3O_2]_2PtCl_4$ requires Pt = 21·5 %).

When a solution of formalin is shaken with triethylphosphine, the latter dissolves, the mixture becomes warm, and all smell of the phosphine disappears, also the solution becomes alkaline, owing to the formation of the quaternary phosphonium hydroxide. On the addition of hydrochloric acid and platinum tetrachloride a crystalline salt is obtained (Found : Pt = 27·4. $[P(C_2H_5)_3CH_3OCl]_2PtCl_4$ requires Pt = 27·6 %).

A similar compound is obtained with acetaldehyde (Found : Pt = 26·5. $[P(C_2H_5)_3C_2H_5OCl]_2PtCl_4$ requires Pt = 26·6 %).

THE RALPH FORSTER LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 19th*, 1925.]

CXXX.—*Derivatives of Semioxamazide. Part III.*

By FORSYTH JAMES WILSON and ERIC CHARLES PICKERING.

IN this communication the action of heat on ketonic semioxamazones is described. From acetophenonesemioxamazone (I) the products were phenylmethylketazine, a little *acetophenoneoxalyldihydrazone* (II), and a mixture of oxamide and *cyclo*oxalylhydrazide. This would indicate that the decomposition of the semioxamazone by heat takes place in two stages—

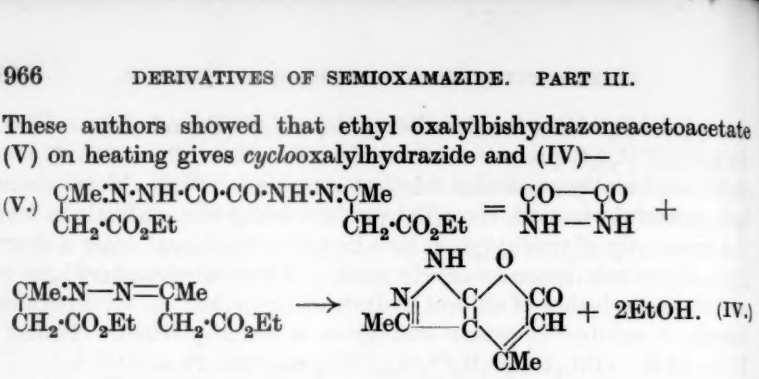
$$\begin{matrix}NH_2\cdot CO\cdot CO\cdot NH\cdot N{:}CMePh\\ NH_2\cdot CO\cdot CO\cdot NH\cdot N{:}CMePh\end{matrix} = \begin{matrix}NH_2\cdot CO\\ NH_2\cdot CO\end{matrix} + \begin{matrix}CO\cdot NH\cdot N{:}CMePh\\ CO\cdot NH\cdot N{:}CMePh\end{matrix}$$

(I.) (II.)

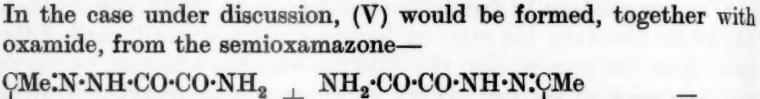
$$\rightarrow \begin{matrix}CO{-}NH\\ CO{-}NH\end{matrix} + \begin{matrix}N{:}CMePh\\ N{:}CMePh\end{matrix}$$

This explanation was confirmed by investigation of the products obtained by heating ethyl acetoacetate semioxamazone (III) at its melting point for several hours. The products isolated were oxamide, *cyclo*oxalylhydrazide, and a substance, m. p. 247°, which proved to be 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone (IV), investigated by Bülow and Lobeck (*Ber.*, 1907, **40**, 708), Bülow and Schaub (*ibid.*, 1908, **41**, 1945) and by Wolff and Schreiner (*ibid.*, 1908, **41**, 550).

These authors showed that ethyl oxalylbishydrazoneacetoacetate (V) on heating gives *cyclo*oxalylhydrazide and (IV)—



In the case under discussion, (V) would be formed, together with oxamide, from the semioxamazone—



The action of heat on the semioxamazones of dibenzyl ketone, acetone, and methyl ethyl ketone was also investigated, the products being the corresponding ketazine, oxamide, and *cyclo*oxalylhydrazide; the intermediate oxalyldihydrazones were not isolated in these cases.

Experimental.

Acetophenonesemioxamazone.—This substance was heated at 215° for 4 hours. The semi-solid mass when cold was powdered and treated with ether, which dissolved phenylmethylketazine; the insoluble residue was repeatedly extracted with boiling absolute alcohol. On cooling, a small quantity of oxamide was deposited from the extract, followed by *acetophenoneoxalyldihydrazone* (described below); concentration of the mother-liquors gave unchanged semioxamazone only.

A portion of the residue left after the alcohol extraction was boiled with sodium hydroxide solution, ammonia being evolved. The residual solution reduced silver nitrate in the cold, indicating the presence of hydrazine, and contained oxalic acid. Another portion was warmed with ammonia solution, in which it was partly soluble; the residue gave ammonia and an oxalate on heating with sodium hydroxide. The ammoniacal solution was made just acid with nitric acid, the white precipitate after filtration was redissolved in ammonia, and silver nitrate added to the solution, neutralised with nitric acid, when the yellow silver derivative of *cyclo*oxalylhydrazide was deposited. These facts indicate that the insoluble product was a mixture of oxamide and *cyclo*oxalylhydrazide (Found: N = 32·9, 31·9. Calc., for oxamide, N = 31·8; for *cyclo*oxalylhydrazide, N = 32·5%).

Acetophenoneoxalyldihydrazone, which has not previously been prepared, was obtained as a crystalline precipitate by boiling

acetophenone and oxalyldihydrazide (mol. quantities) in absolute alcohol with a little iodine, without which no perceptible reaction took place; it separated from alcohol in needles, m. p. 250° (Found: N = 17·0. $C_{18}H_{18}O_2N_4$ requires N = 17·4%).

Ethyl acetoacetate semioxamazone.—The substance was heated at 130–135° for 2 hours, and the semi-solid mass when cold was extracted with boiling absolute alcohol. The insoluble residue was identified in the usual way as a mixture of oxamide and *cyclo*oxalylhydrazide. The alcoholic solution on concentration deposited a substance which after recrystallisation from the same solvent formed prismatic needles, m. p. 247°, and was identified as 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone by analysis (Found: N = 17·30, 17·14. Calc., N = 17·07%) and by comparison with an authentic specimen. Further concentration of the alcoholic extract gave unaltered semioxamazone.

Dibenzyl ketone semioxamazone.—On heating at 200° for 2 hours a little ammonia was evolved and a white sublimate produced. The product was extracted with ether and alcohol successively. The ethereal extract gave dibenzylketazine (m. p. 95—96°); the alcoholic extract contained unaltered substance only. The insoluble residue consisted of oxamide and *cyclo*oxalylhydrazide.

Acetonesemioxamazone.—The dry substance was heated at 180° in a distillation flask arranged as for a vacuum distillation; in 4 hours a small quantity of liquid had distilled over, and more on reducing the pressure slightly. The liquid was dimethylketazine; the residue in the flask, a mixture of oxamide and *cyclo*oxalylhydrazide.

Methyl Ethyl Ketone Semioxamazone.—The reaction was carried out exactly as in the previous case, the products being methylethylketazine, oxamide, and *cyclo*oxalylhydrazide.

In conclusion, we desire to thank the Carnegie Trust for the Universities of Scotland for a grant which has partly defrayed the expenses of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

[*Received, February 21st*, 1925.]

CXXXI.—*Colour and Molecular Geometry. Part III. A Graphical Presentation of the Theory.*

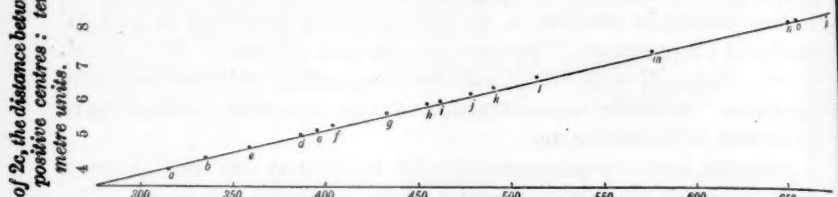
By JAMES MOIR.

THE author's theory of colour is handicapped by the fact that it has a mathematical basis of some complexity, more readily comprehensible by an astronomer than by an organic chemist. He

has therefore presented, by means of a graph, some of the results of the theory.

Even when the hapton * is a derivative of carbon or sulphur, it would appear that in most cases it is the nitrogen or oxygen contained in the hapton that is the active part, *i.e.*, constitutes the second positive centre. A great simplification then arises from the fact that the nitrogen and oxygen atoms have the same size (1·3 Å.) and occur at both ends of the molecule.

FIG. 1.



Calculated position (λ) *of absorption bands. Unit* μμ *or* 10^{-7} *cm.*

References.

a = *Quinol,* p-*aminophenol, and* p-*phenylenediamine.*
b = p-*Diketohexamethylene* (*also free quinonephenylhydrazone*).
c = *Quinoneimine.*
d = p-*Hydroxyazobenzene ion* (*lower band in alkali*).
e = p-*Nitrophenol*, *f* = p-*Nitrosophenol* (*alkaline*).
g = p-*Hydroxyazobenzene ion* (*upper band in alkali*).
h = *Quinone*: *also* p-*nitrophenylhydrazine in alkali.*
i = *Lower band of acidified* p-*hydroxyazobenzene.*
j = *Lower band of acidified aminoazobenzene.*
k = *Upper band of acidified* p-*hydroxyazobenzene.*
l = *Dihydroxyphenazine, diaminophenazine, upper band of acidified aminoazobenzene, azophenol and azoaniline.*
m = *Resorufin.*
n = *Indophenol.*
o = *Indamine.*
p = *Quinhydrone.*

In addition, dihydroxy- and diamino-diphenyl sulphoxide, with λ *about* 750, *fall on the same line with small deviation due to the slightly larger size of the sulphur atom.*

The author's equation

$$\lambda = 112\, a^{3/2} f(e) \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

then becomes [since a is now $(c + 0{\cdot}65)$, and $f(e) = 1{\cdot}249 - 0{\cdot}79c/a$] †

$$\lambda = 51{\cdot}4\ (c + 1{\cdot}77)\sqrt{c + 0{\cdot}65} \quad . \quad . \quad . \quad (II)$$

in which c is half the distance between two positive centres round which the electron moves (two different oxygen or nitrogen atoms). The colour thus depends solely on this distance c.

* For definitions see J., 1923, **123**, 2801.
† See J., 1924, **125**, 1137, 1138.

The graph of this equation over the range of the visible spectrum is practically a straight line. It is shown in Fig. 1 by a series of dots; a straight line is drawn for comparison through the top and bottom results. Each dot corresponds to a coloured substance of which the auxochrome is either –OH or $-NH_2$, and of which the active part of the hapton is oxygen or nitrogen or both.

This approximate proportionality of height of colour (λ) to interfocal distance ($2c$) renders calculation of colour easy. The following table contains some of the data from the graph.

	λ (in $\mu\mu$).			λ (in $\mu\mu$).	
$2c$ (in Å).*	*a*. New equation (II).	*b*. Old equation (I).	$2c$ (in Å).*	*a*. New equation (II).	*b*. Old equation (I).
1·3	142	138	6·0	469	469
2·6	220	218	6·5	510	509
3·9	308	308	7·0	552	550
4·5	352	352	7·5	595	596
5·0	390	390	8·0	640	641
5·5	429	429			

* Contact of the two positive atoms (oxygen or nitrogen).

It would follow that no absorption band lower than λ 138 is possible. Diagrams which are at least plausible have been drawn representing exactly to scale the configurations of all the substances mentioned in Fig. 1. Each diagram has the correct interfocal distance required to give the observed absorption band and, in the author's opinion, represents the real shape and arrangement of the molecules. Physicists may perhaps be astonished at the organic chemist's conception of molecules of such rigid structure; and some organic chemists may be astonished at the conception that the function of the benzene ring in coloured substances is to provide rigidity (and not unsaturation); but the evidence for both conceptions is satisfactory.

Fig. 2 represents ionised quinol, or *p*-phenylenediamine or *p*-aminophenol. The distance between the positive centres ($2c$) is 4·00 Å., corresponding to λ about 315, which is actually possessed by all three substances (as would be expected if oxygen and nitrogen have the same atomic diameter).

Fig. 3 represents *p*-benzoquinone as a flat hexagon with a very slight overlap of the middle carbon atoms at the double bonds. The distance between the oxygen centres is about 5·88 Å., exactly what is required to account for its band at about λ 455.

Fig. 4 represents *p*-diketohexamethylene (*cyclo*hexanedione) as a compromise between the flat hexagon and the skew-hexagon of Bragg. The value of $2c$ is about 4·2 Å. and the absorption band (in presence of alkali) is at λ 335.

Fig. 5 represents *p*-benzoquinoneimine seen sideways. The circle marked X is the hollow centre of the flat benzene ring of quinone (which is of the same size as a carbon atom). The –NH group lies nearly at right angles to the ring. The distance ON (2*c*) is about 4·6 Å., corresponding to λ 365 observed.

Fig. 6 represents two phases of *p*-nitrosophenol (in alkali) in which the oxygen of the nitroso-group can occupy two positions symmetrical about the line of the benzene valency. If the deviation is 45°, the distances O′O″ and O′O are about 3·8 and 5·2 Å., each of which corresponds to an absorption band (observed λλ about 400 and 270).

Fig. 7 represents the skeleton of the parent-substance of *p*-hydroxyazobenzene, $NH{:}N{\cdot}C_6H_4{\cdot}OH$, and is referred to later.

Fig. 8 represents *p*-nitrophenol (in alkali). This, like nitrosophenol, has two bands, λλ about 390 and 238, both of which are correctly predictable from the diagram. The oxygens of the nitro-groups are at right angles to the benzene valency.

Fig. 9 represents *p*-nitrophenylhydrazine (activated by alcoholic potash). The distance between O′ and the farthest N agrees with the absorption band described in Part II of this series.

Fig. 10 represents potassium *p*-nitrophenyldiazotate,

$$NO_2{\cdot}C_6H_4{\cdot}N(OK){:}N \text{ or } NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OK,$$

a substance which is colourless. The small distance between the oxygens of the active groups is a plausible explanation (see addendum to Part II).

Fig. 11 represents the ordinary configuration of *p*-hydroxyazobenzene (in alkali). The distance 5·3 Å. between O′ and N corresponds by calculation to λ 412. This is raised to λ 433 (observed for the *upper* alkali band) by the "loading" of the (inactive) phenyl group. Fig. 12 gives the arrangement for the *lower* alkali band of the same substance ($2c = 4{\cdot}87$ Å., λ about 390).

Fig. 13 gives the probable arrangement for this substance without alkali, when it is very pale and is not ionised. The value of 2*c* is 3·8 Å. Fig. 13A is an azomethine. The colour is lower because the N lies at 125° to carbon as in the hydroxybenzaldehyde.

Fig. 14 attempts to explain both bands of *acidified* *p*-hydroxyazobenzene by representing the active ring as flattened out as in quinone. The distances $ON_{'}$ and $ON_{''}$ are in agreement with the requirements. The same diagram serves for acid *p*-aminoazobenzene, which has two bands slightly higher than those of *p*-hydroxyazobenzene. A very slight rotation of $N_{''}$ relatively to $N_{'}$ is required. The quinonoid configuration $NH{:}C_6H_4{:}N{\cdot}NHPh$ is assumed to exist when the ring is flat.

Fig. 15 represents Chattaway and Clemo's substances (J., 1923,

Fig. 2

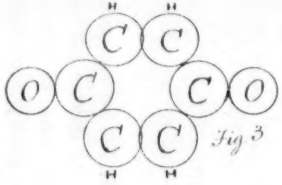


Fig 3

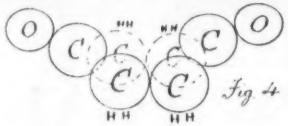


Fig 4

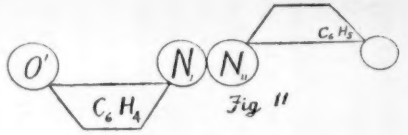


Fig 11

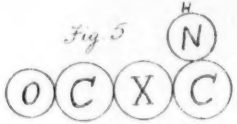


Fig 5

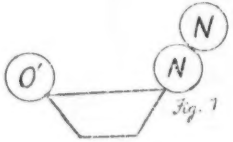


Fig 7

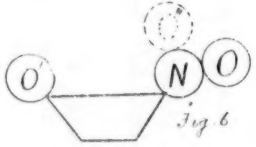


Fig 6

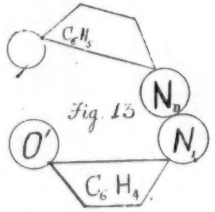


Fig 13

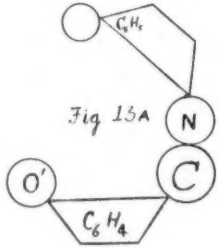


Fig 13A

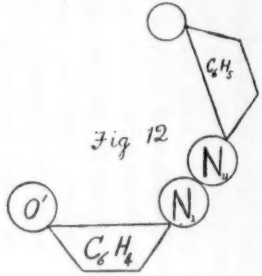


Fig 12

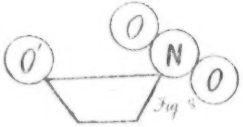


Fig 8

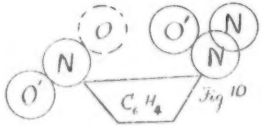


Fig 10

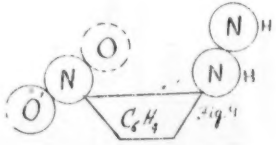


Fig 9

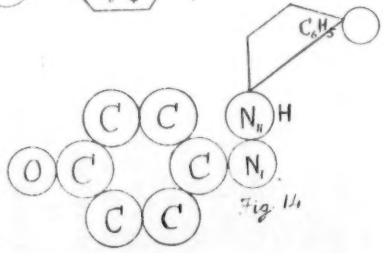


Fig 14

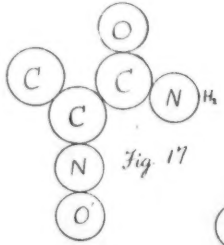


Fig 17

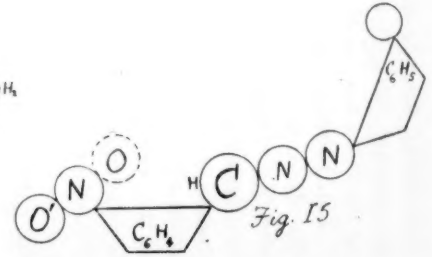


Fig 15

123, 3041), the one of highest colour (*p*-nitrobenzaldehydephenyl. hydrazone) being chosen for this purpose. The distance from O′ to the more remote N is in agreement with the theory.

Fig. 16 represents the configuration of the ion of the violurates, the distance from O′ to the most distant O agreeing with the observed colour (λ 570 when perfectly neutral, rather lower when faintly alkaline). Fig. 17 similarly gives the essential part of the molecule of Whiteley's *iso*nitrosomalonamide (which is yellow when alkaline), a substance obviously connected with the problem of the colour of the violurates.

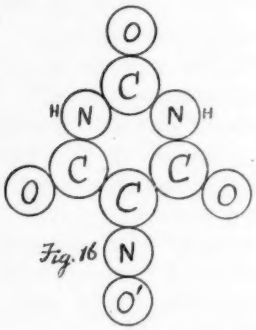


Fig. 16

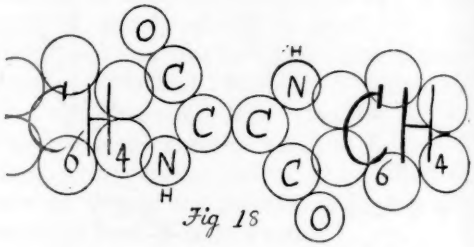


Fig. 18

Fig. 18 represents indigotin. The distance between the two oxygen atoms corresponds to λ about 550. The observed position of the band is λ about 600, and the difference is due to the very oblique position of the two phenylene groups, which is capable (on other evidence) of giving a "loading" of 10%. The view of the C_6H_4 groups is that of the Bragg configuration seen from above.

The configurations of the other substances mentioned in Fig. 1 (such as resorufin) cannot be adequately represented by plane drawings, but agree with the theory.

It is probable that the performance of an orbit by an electron round two positive centres is not only the cause of colour but is the explanation of Lapworth's α—γ tautomerism and of other "balanced" actions. Baly's "isorropesis" is a glimpse of this idea written in pre-electronic days, just as Thiele's "partial valencies" was a prophecy of the linking of two atoms by three electrons.

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CXXXII.—*Studies in the Benzothiazole Series. Part III. The Pseudo-bases of the 1-Substituted Benzothiazole Quaternary Salts.*

By LESLIE MARSHALL CLARK.

THE work of Mills, Clark, and Aeschlimann (J., 1923, **123**, 2353) on the ψ-bases produced by the action of alkalis on the quaternary salts of benzothiazole has now been extended to the quaternary salts of 1-substituted benzothiazoles.

As was to be expected from the previous results, the ψ-bases are substituted thiophenols which are readily oxidised with iodine or atmospheric oxygen to the corresponding disulphides: the identity of these disulphides has been established by direct acylation of 2 : 2′-dimethylaminodiphenyl disulphide with the appropriate acid chloride or anhydride.

The reaction is expressed by the following scheme, R being the substituent radical:

$$C_6H_4\langle\begin{matrix}S\text{—}\\NMeI\end{matrix}\rangle CR \xrightarrow{NaOH} C_6H_4\langle\begin{matrix}SH\\NMe\cdot COR\end{matrix} \xrightarrow{O} \left[C_6H_4\langle\begin{matrix}S-\\NMe\cdot COR\end{matrix}\right]_2$$

The action of formic acid on bis-2-methylbenzothiazoline-1 : 1-spiran (I) confirms the formula assigned to this compound by Mills, Clark, and Aeschlimann (J., 1923, **123**, 2365). When the spiran is boiled with 90% formic acid, 2-methylbenzothiazolone (II) can be isolated from the reaction mixture after partial neutralisation with ammonia. The remaining solution still contains benzothiazole methoformate, since, by making it alkaline with ammonia and exposing to atmospheric oxidation, 2 : 2′-diformylmethylaminodiphenyl disulphide is obtained. This behaviour is characteristic of benzothiazolonium salts (Mills, Clark, and Aeschlimann, *loc. cit.*). Bis-2-methylbenzothiazoline-1 : 1-spiran is therefore hydrolysed by formic acid thus:

$$C_6H_4\langle\begin{matrix}S\text{—}\\NMe\end{matrix}\rangle C\langle\begin{matrix}S\text{—}\\NMe\end{matrix}\rangle C_6H_4 \xrightarrow{H_2O}$$

(I.)

$$C_6H_4\langle\begin{matrix}S\text{—}\\NMe\end{matrix}\rangle CO + C_6H_4\langle\begin{matrix}SH\\NHMe\end{matrix}$$

(II.) (III.)

o-Methylaminophenyl mercaptan (III), which is presumably the second hydrolysis product, is formylated during the reaction to give benzothiazole methoformate (V) by way of the intermediate ψ-base (IV):

$$\text{(III.)} \longrightarrow C_6H_4\langle\begin{matrix}SH\\NMe\cdot CHO\end{matrix} \longrightarrow C_6H_4\langle\begin{matrix}S\\N\end{matrix}\rangle CH \quad \text{(V.)}$$

(IV.)

Me HCO_2

EXPERIMENTAL.

Atmospheric Oxidation of the ψ-Bases.—An aqueous solution of the alkyliodide and 10% ammonia was kept in the dark for 6—8 weeks, when the crystalline deposit was collected.

1-Methylbenzothiazole methiodide (Mills, J., 1922, **121**, 455) (1 g.; water, 10 c.c.; 10% ammonia, 4 c.c.; time, 6 weeks) gave 2 : 2′-*diacetylmethylaminodiphenyl disulphide*, which crystallised from aqueous alcohol in colourless needles (Found: C, 60·1; H, 5·6; N, 7·6. $C_{18}H_{20}O_2N_2S_2$ requires C, 60·0; H, 5·55; N, 7·8%). The same compound was prepared by boiling 2 : 2′-dimethylaminodiphenyl disulphide (Harries and Lowenstein, *Ber.*, 1894, **27**, 867) (0·3 g.) for 5 minutes with acetic anhydride, decomposing the excess of anhydride with water, and crystallising the product from aqueous alcohol (Found: N, 7·9%). Both specimens melted at 171°, alone or mixed.

From 1-methylbenzothiazole ethiodide (3 g.; 10% ammonia, 6 c.c.; time, 2 months) 2 : 2′-*diacetylethylaminodiphenyl disulphide* was obtained which crystallised from light petroleum in colourless needles, m. p. 103° (Found: C, 61·5; H, 6·3; N, 7·25. $C_{20}H_{24}O_2N_2S_2$ requires C, 61·8; H, 6·2; N, 7·2%).

1 : 5-Dimethylbenzothiazole ethiodide (Mills, *loc. cit.*) (1 g.; 10% ammonia, 4 c.c.; time, 2 months) gave 2 : 2′-*diacetylethylamino*-5 : 5′-*dimethyldiphenyl disulphide*, which crystallised from light petroleum in colourless needles, m. p. 129° (Found: C, 63·6; H, 6·8; N, 6·55. $C_{22}H_{28}O_2N_2S_2$ requires C, 63·5; H, 6·7; N, 6·7%).

Titration of 1-*Methylbenzothiazole Ethiodide with Sodium Hydroxide.*—When an aqueous solution of the salt is titrated with sodium hydroxide and phenolphthalein, the red colour of the indicator persists for some seconds after each fresh addition of the alkali, finally fading as the sodium salt of the thiophenol is formed. This time interval becomes so prolonged when nearly the two equivalents of alkali required by theory have been added that a sharp end-point cannot be obtained. 0·2703 G. of the salt required 17·2 c.c. of 0·1*N*-NaOH. Calc., 17·65 c.c.

1-*Phenylbenzothiazole Methiodide.*—1-Phenylbenzothiazole (prepared by heating together a mixture of benzanilide and sulphur) (1·6 g.) was heated with methyl iodide (1·5 g.) at 100° for 24 hours: the solid product, after extraction with ether to remove unchanged base, crystallised from alcohol in yellow plates, m. p. 218° (decomp.) (Found: I, 36·3. $C_{14}H_9NIS$ requires I, 36·3%).

Oxidation of the ψ-Base of 1-*Phenylbenzothiazole Methiodide with Iodine.*—The clear solution obtained from the salt (1·5 g.) and 10% sodium hydroxide (5 c.c.) in water (600 c.c.) was treated slowly

with a solution containing 0·7 g. of iodine. The white precipitate of 2 : 2′-*dibenzoylmethylaminodiphenyl disulphide* crystallised from aqueous alcohol in colourless plates (Found: C, 69·75; H, 5·0; N, 5·8. $C_{28}H_{24}O_2N_2S_2$ requires C, 69·4; H, 5·0; N, 5·8%). The same compound was obtained from 2 : 2′-dimethylaminodiphenyl disulphide, benzoyl chloride, and sodium hydroxide solution. Both specimens melted at 164°, alone or mixed.

Hydrolysis of Bis-2-methylbenzothiazoline-1 : 1-spiran.—The spiran (0·5 g.) was boiled gently for 4½ hours with 90% formic acid (5 c.c.), the solution poured into water and partly neutralised with ammonia, whereby a colourless oil, which eventually solidified, was thrown out. This substance crystallised from light petroleum in clusters of plates. It melted at 76°, alone or mixed with authentic 2-methylbenzothiazolone (m. p. 76°).

The aqueous filtrate was made alkaline with ammonia and kept in the dark for 2 days. The yellow film of solid which had separated was washed, dried, and extracted with light petroleum, in which it was very sparingly soluble. The extracts, on rubbing, slowly deposited small, colourless plates of 2 : 2′-diformylmethylaminodiphenyl disulphide; these melted at 106—107·5°, alone or mixed with an authentic specimen of the disulphide.

I wish to thank Dr. W. H. Mills, F.R.S., for his valuable advice; Mr. F. Flack, who carried out the analyses; and the Department of Scientific and Industrial Research for a grant which enabled this research to be undertaken.

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CAMBRIDGE. [*Received, February 25th,* 1925.]

CXXXIII.—*The Compounds Formed by the Action of Bromine upon Benzaldehydephenylhydrazone.*

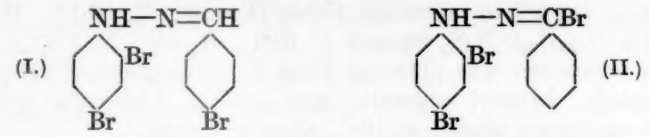
By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

THE bromination of benzaldehydephenylhydrazone was first studied by Ciusa and Vecchiotti (*Gazzetta*, 1916, **46**, i, 240).

From the product obtained when 3 mols. of bromine were added to 1 mol. of the hydrazone in acetic acid solution, they isolated a tribromo-derivative, m. p. 114°.

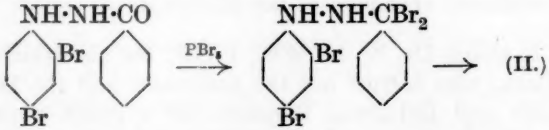
They obtained the same compound by the bromination of the corresponding 2 : 4-dibromophenylhydrazone, and showed that it was not benzaldehyde-2 : 4 : 6-tribromophenylhydrazone, which they prepared from benzaldehyde and 2 : 4 : 6-tribromophenylhydrazine. Since by oxidation of the compound they obtained

p-bromobenzoic acid, they assigned to it the constitution of *p*-bromobenzaldehyde-2 : 4-dibromophenylhydrazone (I).



Humphries, Bloom, and Evans (J., 1923, 123, 1771) have described the same tribromo-derivative, m. p. 114°, and, without referring to the formula previously given by Ciusa and Vecchiotti, regard it as having the structure (II), on the ground that benzophenone-2 : 4-dibromophenylhydrazone is not further brominated under similar conditions.

In the course of an investigation of phenylhydrazones, the action of bromine on benzaldehydephenylhydrazone has been studied, and the constitution of the above product definitely settled in favour of the second alternative, namely, ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone, since the same compound is obtained by the action of phosphorus pentabromide upon β-benzoyl-2 : 4-dibromophenylhydrazine :



The constitution suggested by Ciusa and Vecchiotti has been disproved by the direct preparation of *p*-bromobenzaldehyde-2 : 4-dibromophenylhydrazone from *p*-bromobenzaldehyde and 2 : 4-dibromophenylhydrazine. It is a colourless compound, melting at 126°, and quite distinct in appearance and properties from that obtained by the bromination of benzaldehydephenylhydrazone. The formation of *p*-bromobenzoic acid observed by Ciusa and Vecchiotti must therefore be attributed to the action of bromine liberated during the oxidation.

When boiled for a short time with acetic acid and sodium acetate, ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone is changed almost quantitatively into α-acetyl-β-benzoyl-2 : 4-dibromophenylhydrazine, which yields on hydrolysis acetic acid, benzoic acid, and 2 : 4-dibromophenylhydrazine. The formation of this hydrazide may be represented as an acetylation of the imino-group, and replacement of the methine bromine by hydroxyl :

$$\text{(II.)} \xrightarrow{C_2H_4O_2} C_6H_3Br_2\cdot NAc\cdot N{:}CBrPh \xrightarrow{H_2O}$$
$$C_6H_3Br_2\cdot NAc\cdot N{:}C(OH)Ph \longrightarrow C_6H_3Br_2\cdot NAc\cdot NH\cdot COPh.$$

Its structure is further confirmed by its synthesis from 2 : 4-dibromophenylhydrazine, by benzoylation, followed by acetylation of the product.

The ω-bromine in ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone shows the usual reactivity of halogen in benzal compounds. For example, it reacts readily with ammonia in alcoholic solution to form a hydrazidine, the bromine being replaced by an amino-group :

$$C_6H_3Br_2\cdot NH\cdot N{:}CPhBr \longrightarrow C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot NH_2.$$

When warmed with potassium cyanide in aqueous-alcoholic solution, this bromine is replaced by a cyano-group in a similar manner.

Like ω-chlorobenzaldehydephenylhydrazone, NHPh·N:CPhCl (Pechmann, *Ber.*, 1894, **27**, 322), ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone reacts with phenylhydrazine to give a brightly coloured formazyl derivative :

$$C_6H_3Br_2\cdot NH\cdot N{:}CPhBr \longrightarrow [C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot NH\cdot NHPh] \longrightarrow C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot N{:}NPh.$$

The bright red colour which is produced when ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone alone is warmed with alcoholic potash is probably due to the formation of a similar formazyl compound, the hydrazine in this case being provided by the hydrolysis to benzoic acid and 2 : 4-dibromophenylhydrazine, thus :

$$C_6H_3Br_2\cdot NH\cdot N{:}CPhBr \xrightarrow{HOH} C_6H_3Br_2\cdot NH\cdot NH\cdot COPh \xrightarrow{HOH} C_6H_3Br_2\cdot NH\cdot NH_2 + PhCO_2H,$$

the further reaction of the dibromophenylhydrazine with some of the original substance producing the coloured tetrabromoformazyl compound, $C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot N{:}N\cdot C_6H_3Br_2$.

The presence of sodium acetate in the acetic acid solution during the bromination of benzaldehydephenylhydrazone entirely changes the course of the reaction. When 2 mols. of bromine, 1 mol. of the hydrazone, and an excess of sodium acetate are employed, the product is not ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone, but a sparingly soluble, yellow compound, which has a composition and molecular weight represented by the formula $C_{26}H_{18}N_4Br_2$. This has been shown to be 1 : 4-di-*p*-bromophenyl-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine (III), formed from 2 mols. of the hydrazone as indicated below :

$$\begin{matrix} C_6H_5\cdot CH{:}N\cdot NH\cdot C_6H_5 \\ C_6H_5\cdot NH\cdot N{:}CH\cdot C_6H_5 \end{matrix} \xrightarrow{4Br} \begin{matrix} C_6H_5\cdot C{:}N\cdot N\cdot C_6H_4Br \\ C_6H_4Br\cdot N\cdot N{:}C\cdot C_6H_5 \end{matrix} \quad \text{(III.)},$$

since on dry distillation alone or with zinc dust it yields benzonitrile, whilst energetic reduction gives *p*-bromoaniline, showing that the bromine is in the *p*-position in the nucleus attached to the nitrogen atom.

The compound is also formed by the action of bromine under similar conditions upon either benzaldehyde-*p*-bromophenylhydrazone or ω-chlorobenzaldehydephenylhydrazone:

$$\begin{matrix} C_6H_5\cdot CH{:}N\cdot NH\cdot C_6H_4Br \\ C_6H_4Br\cdot NH\cdot N{:}CH\cdot C_6H_5 \end{matrix} \xrightarrow{2Br_2} \text{(III.)} \xleftarrow{2Br_2} \begin{matrix} C_6H_5\cdot CCl{:}N\cdot NH\cdot C_6H_5 \\ C_6H_5\cdot NH\cdot N{:}CCl\cdot C_6H_5 \end{matrix}$$

The action of bromine upon benzaldehyde-2 : 4-dibromophenylhydrazone in the presence of excess of sodium acetate yields a small amount of the corresponding 2 : 4-dibromo-substituted tetraphenyldihydrotetrazine, $\begin{matrix} C_6H_5\cdot C{:}N\cdot N\cdot C_6H_3Br_2 \\ C_6H_3Br_2\cdot N\cdot N{:}C\cdot C_6H_5 \end{matrix}$, together with a larger amount of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone.

This 1 : 4-di(2 : 4-dibromophenyl)-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine resembles in its yellow colour and reactions the 1 : 4-di-*p*-bromophenyl-3 : 6-diphenyldihydrotetrazine already described.

A mixture of both these derivatives is produced when 3 mols. of bromine are allowed to act upon 1 mol. of benzaldehydephenylhydrazone in the presence of an excess of sodium acetate.

Since in the absence of sodium acetate the product of bromination of benzaldehydephenylhydrazone is the ω-bromo-derivative, $C_6H_3Br_2\cdot NH\cdot N{:}CPhBr$, it is probable that in the presence of sodium acetate the formation of the dihydrotetrazine takes place by the elimination of 2HBr from 2 mols. of an ω-bromo-compound in the following manner:

$$2C_6H_5\cdot NH\cdot N{:}CH\cdot C_6H_5 \xrightarrow{4Br_2} \left[\begin{matrix} C_6H_4Br\cdot NH\cdot N{:}CBr\cdot C_6H_5 \\ C_6H_5\cdot CBr{:}N\cdot NH\cdot C_6H_4Br \end{matrix}\right] \xrightarrow{-2HBr} \begin{matrix} C_6H_4Br\cdot N\cdot N{:}C\cdot C_6H_5 \\ | \\ C_6H_5\cdot C{:}N\cdot N\cdot C_6H_4Br \end{matrix}$$

This would account for the comparatively good yield, and single nature of the product.

Bowack and Lapworth (J., 1905, **87**, 1857) have shown that ω-halogen compounds derived from oxalic acid can be converted into the dihydrotetrazines with great ease by the action of alkalis; *e.g.*,

$$\begin{matrix} C_6H_5\cdot NH\cdot N{:}CBr\cdot CO_2Et \\ EtO_2C\cdot CBr{:}N\cdot NH\cdot C_6H_5 \end{matrix} \longrightarrow \begin{matrix} C_6H_5\cdot N\cdot N{:}C\cdot CO_2Et \\ | \\ EtO_2C\cdot C{:}N\cdot N\cdot C_6H_5 \end{matrix},$$

but so far attempts to obtain tetraphenyldihydrotetrazines in a similar way from either ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone or ω-chlorobenzaldehydephenylhydrazone have failed.

We have already shown that the action of acetic acid and sodium acetate alone upon ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone results in the formation of an acetylbenzoylphenylhydrazine, no dihydrotetrazine being produced, whereas the action of bromine on ω-chlorobenzaldehydephenylhydrazone in the presence of sodium acetate gives a theoretical yield of the *p*-bromo-substituted tetraphenyldihydrotetrazine (III).

It would seem, therefore, that in the formation of the *p*-bromo-substituted tetraphenyldihydrotetrazine from ω-chlorobenzaldehydephenylhydrazone or from benzaldehydephenylhydrazone we cannot regard the substituting action of the bromine and the formation of the heterocyclic ring as two separate and independent processes.

EXPERIMENTAL.

ω-Bromobenzaldehyde-2 : 4-dibromophenylhydrazone (II).—Benzaldehydephenylhydrazone (20 g.) was suspended in 200 c.c. of glacial acetic acid, and a solution of 49 g. (3 mols.) of bromine in acetic acid gradually added. The hydrazone dissolved, and a thick yellow precipitate separated. This is probably an addition compound of bromine with the dibromo-substituted hydrazone, $C_6H_3Br_2 \cdot NH \cdot NBr \cdot CHBrPh$, since on exposure to the atmosphere, or on washing with water, it whitens, losing hydrogen bromide and forming the ω-bromo-compound.

It was separated, washed with water until quite white, and the product recrystallised from acetic acid, separating in long, colourless needles, m. p. 114° (Found : Br, 55·5. Calc., Br, 55·4%).

Preparation of ω-Bromobenzaldehyde-2 : 4-dibromophenylhydrazone from β-Benzoyl-2 : 4-dibromophenylhydrazine by the Action of Phosphorus Pentabromide.—To 3·5 g. (1 mol.) of β-benzoyl-2 : 4-dibromophenylhydrazine dissolved in 15 g. (6 mols.) of phosphorus tribromide,* 8 g. (2 mols.) of phosphorus pentabromide were added, and the mixture was warmed gently on a water-bath. The reddish-brown viscid liquid that remained when the evolution of hydrogen bromide had ceased was dissolved in ether, and the solution gradually added to 50 c.c. of methyl alcohol. The ether was evaporated off, and on cooling the resulting alcoholic solution a mass of fine crystals separated. These were recrystallised from acetic acid. They proved to be identical in appearance, properties, and melting point (114°) with the bromination product of benzaldehydephenyl-

* β-Benzoyl-2 : 4-dibromophenylhydrazine does not react with phosphorus tribromide even when boiled with it, at 170°, for some hours. The use of the pentabromide alone is not desirable, since at 100° it is appreciably dissociated into the tribromide and free bromine. The presence of an excess of the tribromide almost entirely prevents this.

hydrazone. Yield, 1 g. A little of the substance treated with ammonia in alcoholic solution yielded benzaldehyde-2 : 4-dibromophenylhydrazidine, m. p. 115° (p. 981).

p-*Bromobenzaldehyde-2 : 4-dibromophenylhydrazone.* — *p*-Bromobenzaldehyde (2 g.), prepared from *p*-bromotoluene by the Etard method (*Ber.*, 1896, **29**, 153), was added to a hot solution of 3 g. of 2 : 4-dibromophenylhydrazine hydrochloride and 1 g. of sodium acetate in acetic acid. On cooling, the hydrazone separated as a pulp of fine crystals. It crystallised from alcohol in fine, white needles, m. p. 126° (Found: Br, 55·65. $C_{13}H_9N_2Br_3$ requires Br, 55·4%).

A mixture of this compound with ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone (m. p. 114°) melted at 95°.

Reaction of ω-Bromobenzaldehyde-2 : 4-dibromophenylhydrazone with Sodium Acetate and Acetic Acid.—A mixture of 5 g. of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone and 5 g. of fused and powdered sodium acetate was boiled with 100 c.c. of acetic acid. Sodium bromide slowly separated, and after 2 hours the colourless solution was cooled and poured into water. The white, amorphous precipitate crystallised * from alcohol in short, colourless, well-developed prisms, m. p. 158—159°. It is easily soluble in acetic acid, chloroform, or benzene. An analysis showed that one bromine of the original compound had been replaced by the group $C_2H_3O_2$ (Found: Br, 38·9%. $C_{15}H_{12}O_2N_2Br_2$ requires Br, 38·8%).

Two g. of the substance were boiled for 2 hours with a mixture of 20 c.c. of alcohol and 20 c.c. of concentrated hydrochloric acid. The colourless solution on cooling deposited long, white needles, which were shown to be the hydrochloride of 2 : 4-dibromophenylhydrazine by conversion into the characteristic bright red *o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone, m. p. 205°.

The mother-liquor from the hydrolysis, which smelt strongly of ethyl acetate, was made slightly alkaline with caustic soda, and the alcohol distilled off. The resulting solution was acidified with hydrochloric acid, and allowed to cool, when colourless crystals of benzoic acid (m. p. 121°) separated. The hydrolysis of the compound in this way to 2 : 4-dibromophenylhydrazine, acetic acid, and benzoic acid indicated that it was probably an acetylbenzoyl-2 : 4-dibromophenylhydrazine, $C_6H_3Br_2{\cdot}NAc{\cdot}NH{\cdot}COPh$. This constitution was further established by the direct synthesis of the compound from 2 : 4-dibromophenylhydrazine.

* The amorphous solid first formed melts indefinitely below 100° and is extremely soluble in most organic solvents. In recrystallising, it was essential to seed the solution with crystals previously obtained by allowing a little of the substance to stand in contact with a few drops of acetic acid for some days.

This hydrazine (5 g.) was benzoylated by the method of Schotten and Baumann. The insoluble product, β-benzoyl-α-2 : 4-dibromophenylhydrazine, $C_6H_3Br_2 \cdot NH \cdot NH \cdot CO \cdot C_6H_5$, crystallised from alcohol in colourless needles, m. p. 172° (Found : Br, 43·25. $C_{13}H_{10}ON_2Br_2$ requires Br, 43·2%). The acetyl derivative, prepared by boiling 1 g. of this compound for a few minutes with equal parts of acetyl chloride and acetic acid, was identical in melting point (158—159°), appearance, and properties with, and did not depress the melting point of, the substance obtained from ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone.

Benzaldehyde - 2 : 4 - dibromophenylhydrazidine. — Concentrated aqueous ammonia (5 c.c.) was added to a suspension of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone (5 g.) in 50 c.c. of alcohol, and the mixture gently warmed until all had dissolved. The light brown solution was poured into water, when the hydrazidine slowly separated as a semi-solid mass, which was recrystallised from alcohol. It separated in colourless, compact, six-sided prisms, m. p. 115°. It is easily soluble in most organic solvents, sparingly soluble in ligroin, and insoluble in water (Found : Br, 43·4. $C_{13}H_{11}N_3Br_2$ requires Br, 43·3%).

The hydrochloride of this hydrazidine, obtained by cooling a hot solution of 5 g. of the base in 50 c.c. of alcohol and an equal volume of concentrated hydrochloric acid, forms glistening, white, rectangular plates, m. p. 260° (decomp.). It is moderately soluble in alcohol and sparingly soluble in water (Found : Cl + Br, 47·9. $C_{13}H_{12}N_3ClBr_2$ requires Cl + Br, 48·2%).

The constitution of this hydrazidine was confirmed by its synthesis from ω-chlorobenzaldehydephenylhydrazone.

The hydrazone (5 g.), prepared from phosphorus pentachloride and β-benzoylphenylhydrazine by Pechmann's method (*Ber.*, 1894, 27, 2122), was suspended in acetic acid and a solution of 8 g. (2 mols.) of bromine in acetic acid slowly added. The yellow precipitate of *ω-chlorobenzaldehyde-2 : 4-dibromophenylhydrazone* crystallised from acetic acid in colourless needles, m. p. 109° (Found : Cl + Br, 50·45. $C_{13}H_9N_2ClBr_2$ requires Cl + Br, 50·2%).

The action of ammonia upon it is precisely similar to its action upon the ω-bromo-compound, benzaldehyde-2 : 4-dibromophenylhydrazidine being formed.

ω-Cyanobenzaldehyde-2 : 4-dibromophenylhydrazone,

$$C_6H_3Br_2 \cdot NH \cdot N{:}CPh \cdot CN.$$

—A solution of 5 g. of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone in 50 c.c. of boiling alcohol was boiled with a solution of 2 g. of potassium cyanide in 5 c.c. of water for ½ hour, and on cooling, faintly yellow crystals of the cyano-compound separated.

They were washed with a little hot water, dried, and recrystallised from boiling alcohol, in which they were moderately soluble.

This compound is polymorphic, and separates from alcoholic solutions first in long, pale yellow, hair-like crystals, which fill the entire liquid. These, if left in the solvent at the ordinary temperature, slowly redissolve, transforming into stouter crystals of a somewhat deeper shade of yellow, which finally sink to a compact layer upon the bottom of the containing vessel. The complete transformation requires about 2 days. Both forms melt at 139° (Found: Br, 42·3. $C_{14}H_9N_3Br_2$ requires Br, 42·2%).

Dibromoformazylbenzene, $C_6H_3Br_2{\cdot}NH{\cdot}N{:}CPh{\cdot}N{:}NPh$.—To 5 g. (1 mol.) of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone suspended in 50 c.c. of alcohol, an excess, 5 g., of phenylhydrazine was added, and the mixture boiled for 15 minutes. The solution quickly developed a deep red coloration, and dark crystals of the formazyl derivative separated. It crystallised from boiling acetic acid in small clusters of reddish-brown needles, m. p. 173—174° (Found: N, 12·4; Br, 35·0. $C_{19}H_{14}N_4Br_2$ requires N, 12·2; Br, 34·9%).

Formation of Substituted Tetraphenyldihydrotetrazines. 1 : 4-*Di*-p-*bromophenyl*-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine* (III).—Twenty g. (1 mol.) of benzaldehydephenylhydrazone and 40 g. (5 mols.) of fused and finely powdered sodium acetate were made into a thin paste with acetic acid, cooled, and a solution of 32 g. (2 mols.) of bromine in 50 c.c. of acetic acid added in small portions. The yellow solution slowly deposited a mixture of sodium bromide and fine yellow crystals of the dihydrotetrazine. After a few hours, the precipitate was collected, washed with hot water, and recrystallised from acetic acid, separating very slowly in well-formed, bright yellow prisms, m. p. 265°: Yield 13 g., 50% of the theoretical. The tetrazine is almost insoluble in alcohol or ligroin, and only moderately soluble in benzene or chloroform (Found: C, 57·6; H, 3·5; N, 10·3; Br, 29·3; *M*, cryoscopic in benzene, 535. $C_{13}H_9N_2Br$ requires C, 57·15; H, 3·3; N, 10·3; Br, 29·2%; *M*, 546).

The substance dissolves in concentrated sulphuric acid, giving a yellow solution, which changes to deep blue when a trace of nitric acid or other oxidising agent is added. When energetically reduced in acetic acid solution by concentrated hydrochloric acid and zinc, a clear solution was obtained which yielded *p*-bromoaniline on making alkaline and steam distilling.

On strongly heating above its melting point, it decomposed and benzonitrile (b. p. 188°, yielding benzoic acid on hydrolysis) distilled over. When an intimate mixture of the compound with

zinc dust (4 parts) was distilled in the same way, benzonitrile distilled over as before, and in addition a quantity of ammonia was evolved.

Preparation of 1 : 4-*Di*-p-*bromophenyl*-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine* (a) *from Benzaldehyde*-p-*bromophenylhydrazone.*—To a solution of 2·7 g. (1 mol.) of benzaldehyde-*p*-bromophenylhydrazone and 6 g. of powdered anhydrous sodium acetate in 100 c.c. of acetic acid, a solution of 1·6 g. (1 mol.) of bromine in acetic acid was gradually added. The solution on standing deposited fine, yellow crystals which when washed free of sodium bromide and recrystallised from acetic acid melted at 265°, and were identical in appearance and properties with 1 : 4-di-*p*-bromophenyl-3 : 6-diphenyl-1 : 4-dihydrotetrazine (m. p. 265°) prepared from benzaldehydephenylhydrazone. Yield 1 g.

(b) *From ω-Chlorobenzaldehydephenylhydrazone.*—To a fine suspension of 6 g. (1 mol.) of the hydrazone and 10 g. (5 mols.) of fused and powdered sodium acetate in acetic acid, a solution of 4 g. (1 mol.) of bromine in acetic acid was slowly added, a light brown solution being formed. This, on standing, deposited a mixture of sodium bromide and yellow crystals of the dihydrotetrazine. These were washed first with a little alcohol and then with hot water, and dried. The compound was practically pure, and the yield, 6 g., 90% of the theoretical.

Preparation of 1 : 4-*Di*(2 : 4-*dibromophenyl*)-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine from Benzaldehyde*-2 : 4-*dibromophenylhydrazone.*—A solution of 2 g. (1 mol.) of bromine in acetic acid was added to a suspension of 5 g. (1 mol.) of benzaldehyde-2 : 4-dibromophenylhydrazone and 10 g. of fused and powdered sodium acetate in the same solvent. The hydrazone dissolved, and white crystals of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone separated. No dihydrotetrazine could be isolated, and the sodium acetate did not appear to have affected the normal course of the reaction.

The use of a larger proportion of bromine, however, under similar conditions resulted in the formation of small quantities of the dihydrotetrazine.

Five g. (1 mol.) of benzaldehyde-2 : 4-dibromophenylhydrazone and 10 g. of sodium acetate were made into a fine paste with acetic acid, and 4 g. (2 mols.) of bromine in acetic acid were gradually added. The hydrazone dissolved and towards the end of the addition a thick, yellow precipitate separated. This was washed with water, and extracted with 50 c.c. of boiling alcohol, when the greater part passed into solution, leaving a fine, yellow, insoluble residue. The hot alcoholic solution, on cooling, deposited colourless crystals of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone,

m. p. 114°. The yellow residue crystallised from acetic acid, in which it was somewhat sparingly soluble, in glistening, irregular, pale yellow leaflets, m. p. 255°. Yield 0·6 g. The use of a larger proportion of bromine did not improve the yield further. The compound is almost insoluble in alcohol or ligroin, and only moderately soluble in benzene or chloroform (Found: N, 7·8; Br, 45·4; *M*, ebullioscopic in chloroform, 674. $C_{26}H_{16}N_4Br_4$ requires N, 8·0; Br, 45·4%; *M*, 704).

Like the corresponding *p*-bromophenyl-compound described above, it dissolves in sulphuric acid, giving a yellow solution which changes to a vivid blue when an oxidising agent is added. It decomposes in a similar manner on dry distillation, yielding benzonitrile, showing that no substitution has taken place in the original benzaldehyde nucleus.

Formation of 1 : 4-*Di*-p-*bromophenyl- and* 1 : 4-*Di*(2 : 4-*dibromophenyl*)-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine by the Action of Bromine* (3 *mols.*) *upon Benzaldehydephenylhydrazone in Presence of Sodium Acetate.*—When to the yellow mixture obtained by adding 32 g. (2 mols.) of bromine to 20 g. (1 mol.) of benzaldehydephenylhydrazone and 40 g. of sodium acetate in acetic acid, a further 16 g. (1 mol.) of bromine dissolved in acetic acid were added, the solution darkened, and a blackish solid was deposited. This was separated, washed with hot water, and dissolved in about a litre of boiling acetic acid. A dark solution was formed and some bromine vapour was evolved. On cooling, a mixture of the two bromo-substituted tetraphenyldihydrotetrazines was deposited as yellow crystals. After four recrystallisations from boiling acetic acid the di-*p*-bromophenyldiphenyldihydrotetrazine (m. p. 265°) was obtained in a pure condition (yield 3—4 g.). The mother-liquors from the first of these operations were diluted with alcohol, and on standing deposited light yellow leaflets of the di(2 : 4-dibromophenyl)diphenyldihydrotetrazine, together with a few heavier compact prisms of the preceding dihydrotetrazine. A rough separation was effected by mechanically washing off the lighter leaflets with a little alcohol, and these were then purified by four recrystallisations from acetic acid. Yield, nearly 0·5 g. The product thus obtained melted at 255°, and proved to be identical with 1 : 4-di(dibromophenyl)-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine obtained from benzaldehyde-2 : 4-dibromophenylhydrazone.

THE QUEEN'S COLLEGE, OXFORD. [*Received, February* 12*th*, 1925.]

CXXXIV.—*Ring-chain Tautomerism. Part XIII. Three-carbon Ring-chain Tautomerism in a Bridged Ring System.*

By JOHN WILLIAM BAKER.

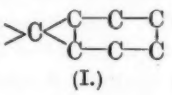
IT has been pointed out (Ingold, Perren, and Thorpe, J., 1922, **121**, 1765) that whenever the groups $>C(CO_2Et)\cdot CO_2Et$ and $[H]C(CO_2Et)\cdot CO_2Et$ required for Michael's addition reaction are present in the same molecule, three-carbon tautomerism may result. The tautomeric change is of the glutaconic type (A) or of the ring-chain three-carbon type (B) according as the groups are contiguous or not.

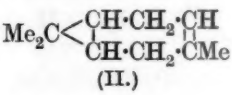
$$CO_2Et\cdot[H]C\!-\!C(CO_2Et)\cdot CO_2Et \rightleftharpoons CO_2Et\cdot C\!=\!C\cdot C[H]\cdot CO_2Et \quad (A)$$

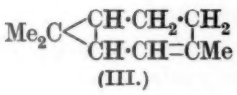
$$CO_2Et\cdot[H]C\!<^{[CH_2]_n}\!>C(CO_2Et)\cdot CO_2Et \rightleftharpoons CO_2Et\cdot C\!<^{[CH_2]_n}\!>C\cdot C[H]\cdot CO_2Et \quad (B)$$

The reaction of type B for which $n = 2$ has already been investigated (*loc. cit.*). The examination of the simpler type ($n = 1$) forms the subject of this paper.

In all experiments of this kind a difficulty arises from the instability of the alicyclic ring when an easy path is provided for its fission. This may be overcome (as has previously been shown) by the introduction of bulky substituents, but in the present case the device was adopted of enclosing two of the valencies of the *cyclo*propane ring in a *cyclo*hexane ring; the stability of the structure (I) thus produced appears to be guaranteed by the occurrence of Δ^3- and Δ^4-carene (II and III) in nature (Simonsen, J., 1920, **117**, 570; 1922, **121**, 2292).


(I.)

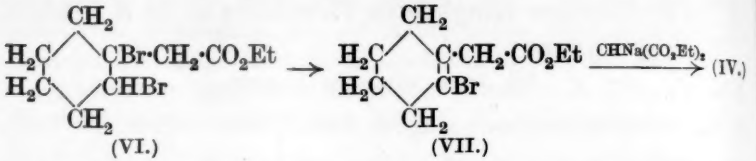

(II.)


(III.)

Since carene on treatment with an ethereal solution of hydrogen chloride is converted into sylvestrene hydrochloride, fission of the *cyclo*propane ring occurring, the existence of tautomeric interchange between the *cyclo*hexene derivative (IV) (p. 987) and the *bicyclo*heptane compound (V) seemed highly probable.

A rational synthesis of the unsaturated, open-chain form (IV) of the ester was effected by condensing the dibromo-addition product of ethyl Δ^1-*cyclo*hexeneacetate (VI) with sodiomalonic ester. The first action appears to be the elimination of hydrogen bromide with the formation of the bromo-compound (VII) (which

was isolated), and this, reacting with a molecule of sodiomalonic ester, yields the required Δ^1-*cyclo*hexene-1-acetate-2-malonate (IV).

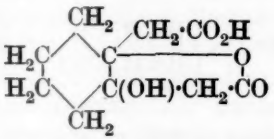


Clear evidence of the existence of ring-chain tautomerism in this ester has been obtained, since, under different conditions, unsaturated products derived from the open-chain form (IV) and saturated products derived from the dicyclic form (V) were isolated in yields which exclude the possibility that the ester is merely a static mixture of the two forms.

Hydrolysis of the parent ester (IV or V) with 4*N*-alcoholic potash yields the *unsaturated*, tricarboxylic acid (VIII), derived from the open-chain form, the yield, after purification, amounting to 69%, calculated on the assumption that the ester exists entirely in its unsaturated form. On regulated oxidation with an alkaline solution of permanganate in the cold, this acid yields a lactone derivative (IX) of the dihydroxy-acid, which can also be isolated, in small yield as a by-product, from the gum obtained as the product of hydrolysis of the ozonide of the parent ester; and, in the latter case, the absence of any side-chain fission products proves that the double bond is not extracyclic.

On the other hand, hydrolysis of the parent ester (IV) or (V) with 20% hydrochloric acid yields the fully *saturated* dicarboxylic acid (X) corresponding to the dicyclic form of the ester, carbon dioxide having been eliminated during the hydrolysis.

(IX.)



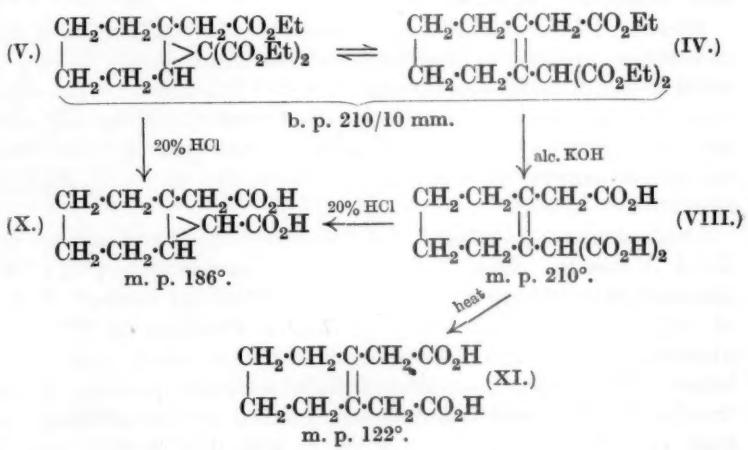
This acid is only slowly attacked even by boiling potassium permanganate in acid solution, and the yield of crystalline material amounts to 34%, calculated on the assumption that the ester existed entirely in its dicyclic form (V). The combined yields of the two acids resulting, respectively, from the hydrolysis of the open-chain and dicyclic forms of the ester amount to more than 100%, thus excluding any possibility that the parent ester is a static mixture of the two forms.

On treatment with 20% hydrochloric acid the *unsaturated*,

tricarboxylic acid (VIII) is converted into the *saturated*, dicarboxylic acid (X), this reagent being capable of effecting the irreversible change between the two solid acids which is analogous to the reversible change producing tautomeric equilibrium in the liquid ester.

On fusion, the tricarboxylic acid (VIII) loses a molecule of carbon dioxide and is converted, not into the saturated acid (X), but, mainly at least (see footnote, p. 990) into an isomeric, unsaturated acid (XI).

These results, which are summarised below, can be explained only by the existence, in the parent ester, of a tautomeric equilibrium such as was previously postulated between open-chain and dicyclic forms.



In such a case it would seem possible to estimate the quantity of unsaturated form present by titrating the ester with a standard solution of bromine; this, by removing the unsaturated individual, would disturb the equilibrium, and an initial rapid absorption should be followed by a slower absorption as the equilibrium is re-established with the formation of a further quantity of the unsaturated form. Since, however, no such clear line of demarcation between rapid and slower absorption of bromine could be observed (bromine being fairly rapidly absorbed until the theoretical quantity for 100% of the unsaturated form of the ester had been added), it must be concluded, either that the re-establishment of the equilibrium is too rapid for detection by this method, or that the equilibrium is largely displaced in favour of the unsaturated form. In the latter case the formation of the saturated acid to the extent of 34% can be accomplished only by the con-

version of a large quantity of the unsaturated ester into its saturated, dicyclic form, and thus, in the opinion of the author, the existence of ring-chain tautomerism of the three-carbon type has been experimentally established in what is essentially the simplest possible case, using the *cyclo*hexane ring as the stabilising influence on the attached *cyclo*propane ring.

EXPERIMENTAL.

Ethyl Δ^1-*cyclo*hexeneacetate was prepared by condensing *cyclo*hexanone with bromoacetic ester and zinc in benzene solution (Reformatsky's method), and dehydrating the hydroxy-ester by heating with powdered, fused potassium hydrogen sulphate. The product was fractionated and the fraction, b. p. 118—125°/20 mm., used in this investigation.

Ethyl 1 : 2-*Dibromo*cyclo*hexane*-1-*acetate* (VI).—A solution of 20 g. of bromine in 120 c.c. of chloroform was added slowly to 20 g. of ethyl Δ^1-*cyclo*hexeneacetate cooled in ice. The solvent was evaporated in a vacuum at the ordinary temperature, and the last traces were removed in a vacuum desiccator over potash. The crude substance cannot be distilled (Found: Br, 49·5. $C_{10}H_{16}O_2Br_2$ requires Br, 48·9%).

Condensation of Ethyl 1 : 2-*Dibromo*cyclo*hexane*-1-*acetate with Ethyl Malonate. Ethyl* 2-*Bromo*-Δ^1-cyclo*hexeneacetate* (VII).—The dibromo-ester (49 g.) was added to a well-cooled mixture of 24 g. of ethyl malonate and 6·9 g. of sodium dissolved in 150 c.c. of absolute alcohol, and the whole was heated under reflux for 3 hours. The product, separated from a small quantity of acid fraction in the usual manner, was purified by fractionation in a high vacuum, and the fraction, b. p. 128—135°/8 mm., was collected (Found: C, 48·9; H, 6·6; Br, 31·4. $C_{10}H_{15}O_2Br$ requires C, 48·6; H, 6·1; Br, 32·4%).

Ethyl Δ^1-cyclo*Hexene*-1-*acetate*-2-*malonate* (IV). — The bromo-compound (VII) (30 g.) was condensed with 30 g. of ethyl malonate and 4 g. of sodium dissolved in 100 c.c. of absolute alcohol. The product, worked up as before, was a rather viscous, almost colourless oil, b. p. 210°/10 mm. (Found: C, 60·9; H, 7·95. $C_{18}H_{26}O_6$ requires C, 60·9; H, 8·0%).

(a) *Hydrolysis with alcoholic potash.* The ester (IV) (15 g.) was heated under reflux with a solution of 12 g. of potassium hydroxide in 75 c.c. of 95% alcohol for several hours. After extraction of the organic acid in the usual manner, Δ^1-cyclo*hexene*-1-*acetic*-2-*malonic acid* (VIII) was obtained from the ethereal solution as a slightly viscous solid (11·5 g.), from which gummy impurities were removed by repeated extraction with hot benzene. The white,

solid residue melted at 210° after repeated crystallisation from acetone–chloroform (Found: C, 54·4; H, 5·8; *M*, by titration, 242·7. $C_{11}H_{14}O_6$ requires C, 54·55; H, 5·8%; *M*, 241·8).

(b) *Hydrolysis with 20% hydrochloric acid.* The ester (IV) (2·8 g.) was heated under reflux with 40 c.c. of 20% hydrochloric acid for 20 hours. On cooling, the main portion of the acid product (0·5 g.) crystallised. The mother-liquor, on extraction with ether, yielded a gum which slowly deposited a further 0·1 g. of the acid. On recrystallisation from acetone–chloroform, 2-*carboxy*bicyclo-[4,1,0]*heptane*-1-*acetic acid* (X) was obtained as small rosettes, m. p. 186°. It does not decolorise an alkaline solution of potassium permanganate, or a solution of bromine in chloroform (Found: C, 60·4; H, 7·0. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). On titration it behaved as a monobasic acid; *M*, 196·5 (*M*, calculated for a dibasic acid, 99·0).

Conversion of the Open-chain Unsaturated Acid into the Dicyclic Saturated Acid.—The unsaturated acid (VIII) (0·2 g.) was heated under reflux with 15 c.c. of 20% hydrochloric acid for 24 hours. On cooling, a small quantity of slightly brown, crystalline material separated, which, when purified on porous porcelain, had m. p. 182°, and was proved by its properties and by means of a mixed melting-point determination with a genuine specimen to be the saturated, dicyclic acid (X).

Oxidation of Δ^1-cyclo*Hexene*-1-*acetic*-2-*malonic Acid. Lactone of* 1 : 2-*Dihydroxy*cyclo*hexane*-1 : 2-*diacetic Acid* (IX).—A solution of 1 g. of the acid in 30 c.c. of sodium bicarbonate solution was cooled in ice, and 145 c.c. of *N*/8-potassium permanganate added slowly with constant shaking. After several extractions of the precipitated hydrated manganese dioxide with boiling water, the combined filtrates were concentrated and extracted with ether. The residue from the dried ethereal solution solidified to an almost gum-free mass which, after several crystallisations from ethyl acetate–petroleum (b. p. 60—80°), was obtained in minute needles, m. p. 187° (Found: C, 54·8; H, 6·5. $C_{10}H_{14}O_5$ requires C, 56·0; H, 6·6%). Since there was a possibility of carbon dioxide splitting off incompletely during the experiment, the product was probably contaminated with the lactone of 1 : 2-dihydroxy*cyclo*hexane-1-acetic-2-malonic acid (which requires C, 51·2; H, 5·4%), but with the quantity of material available, complete separation of these two acids by fractional crystallisation was impossible. The presence of a small quantity of the latter would explain the low percentage of carbon obtained in the analysis.

Oxidation of Ethyl Δ^1-cyclo*Hexene*-1-*acetate*-2-*malonate by Ozone.*—When the ozonide obtained from the parent ester was hydrolysed,

no fission products could be detected, the same lactone being the sole product identified.

Δ^1-cyclo*Hexene*-1 : 2-*diacetic Acid* (XI).—This acid is obtained as the chief product * when the acid (VIII) is heated at 215° for 15 minutes. The clear brown gum obtained from about 1 g. dissolved readily, with effervescence, in sodium carbonate solution. The acid, extracted by ether, on recrystallisation from dry benzene, was obtained in small prisms, m. p. 122° (Found: C, 59·9; H, 7·2; *M*, by titration, 192. $C_{10}H_{14}O_4$ requires C, 60·4; H, 7·0%; *M*, 198).

Titration of the Parent Ester with Bromine.—An *N*/5-solution of pure bromine in chloroform was added from a burette to 0·937 g. of the ester. The rate of absorption, which was very rapid at first, gradually decreased. When 30 c.c. of the bromine solution had been added, the colour persisted for a long period, hydrogen bromide being slowly given off. The unsaturated form of the ester would require 29·63 c.c. for 0·937 g.

The author wishes to express his gratitude to Prof. C. K. Ingold for suggesting this research and for his valuable advice during its progress.

THE UNIVERSITY, LEEDS. [*Received, February 26th,* 1925.]

CXXXV.—*Synthesis of* 5 : 5′-*Dibromo*-6 : 6′-*dimethoxy*-2 : 2′-*bisoxythionaphthen.*

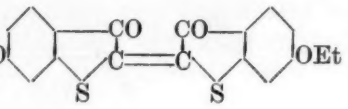
By ROLAND HALL GRIFFITH and EDWARD HOPE.

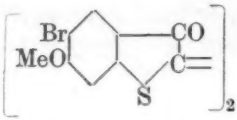
IN connexion with investigations carried out at various times by one of us on the relation between colour and orientation of substituents in certain types of thioindigoid dyes, the need for more accurate information than any then available became evident.

It is well known that 6 : 6′-diethoxy-2 : 2′-bisoxythionaphthen (I) ("6 : 6′-Diethoxythioindigo," Helindone Orange R) passes on dibromination into "Helindone Fast Scarlet R"; it is extremely probable that the position of entry of the bromine atoms is either 5 : 5′ or 7 : 7′, but in view of the interesting and marked changes in colour which are known to occur among "thioindigo" derivatives it was desirable to obtain definite evidence. It was further

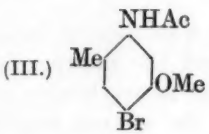
* In one or two experiments very small quantities of two other acids, both unsaturated, with m. p.'s 147° and approximately 180°, respectively, were obtained, but not in sufficient quantities for investigation.

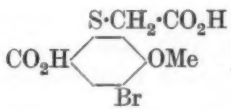
worth while to attempt to discover whether, in the event of substitution occurring in one of the likely positions 5 and 7, any difference of colour would be noticeable if 5 were preferred to 7.

(I.) 


(II.)

The present communication deals with the synthesis of the compound (II) and describes a number of new derivatives of *p*-tolyl methyl ether. The starting point was *p*-tolyl carbonate, which was nitrated so as to yield, after hydrolysis of the product, 2-nitro-*p*-cresol. This was converted by well-known processes into 5-bromo-2-acetylamino-*p*-tolyl methyl ether (III). After oxidation of the latter to 5-bromo-2-acetylamino-4-methoxybenzoic acid, this substance was converted by the well-known process (D.R.-P. 205450) into 4-bromo-2-carboxy-5-methoxyphenylthiolacetic acid (IV) and thence into the corresponding "thioindigo."

(III.) 


(IV.)

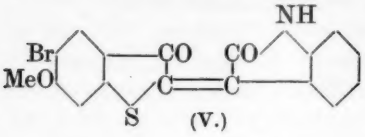
The constitution of the substance (III) was definitely established by elimination of the acetylamino-group and oxidation of the resulting bromomethylanisole to 3-bromoanisic acid; the 2-bromo-acid was also prepared for comparison.

The bromoacetylaminomethoxybenzoic acid obtained by the oxidation of (III) loses carbon dioxide with great ease on boiling with hydrochloric acid; the anthranilic acid has to be prepared by means of alkali. This loss of carbon dioxide is of interest in connexion with the statement of Friedländer (*Annalen*, 1912, **388**, 48) that 4-methoxyanthranilic acid is stable in boiling hydrochloric acid, whereas 6-bromoanthranilic acid loses carbon dioxide like the one here described.

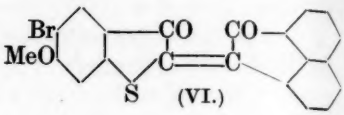
5:5′-Dibromo-6:6′-dimethoxy-2:2′-bisoxythionaphthen (II) is a dye of pure scarlet colour indistinguishable from Helindone Scarlet R. Their absorption spectra are so similar as to suggest an identical constitution. It may be that the replacement of the methoxy-group in (II) by an ethoxy-group will produce a dye with an absorption band identical with that of Helindone Scarlet.

In addition to the "thioindigo," two other dyes have been obtained from the acid (IV); condensation with isatin yields the

substance (V) and a similar reaction with acenaphthenequinone gives the "indigo" (VI).



(V.)



(VI.)

EXPERIMENTAL.

*2-Acetylamino-*p*-tolyl Methyl Ether.*—The reduction of 2-nitro-*p*-tolyl methyl ether, which was effected by Limpach with tin and hydrochloric acid (*Ber.*, 1891, **24**, 4140), is more conveniently done with iron and acetic acid. A mixture of 15 g. of the nitro-ether, 4 c.c. of glacial acetic acid, and 250 c.c. of water is stirred to give an emulsion, and iron filings are added at about 70°, at such a rate that the temperature remains at 80—90°. When the reaction is complete the mixture is cooled and extracted with benzene. The crude amine is distilled under reduced pressure; b. p. 140°/20 mm., m. p. 47°.

Acetic anhydride (1·1 equivs.) is added to a solution of the amine in benzene–light petroleum (b. p. 80°), and the mixture heated on a water-bath until reaction begins. The 2-acetylamino-*p*-tolyl methyl ether remaining after removal of the solvent is distilled under reduced pressure; b. p. 109°/15 mm., m. p. 96° (compare Friedländer, *loc. cit.*).

Bromination.—The acetyl compound (9 g.) is dissolved in 90 g. of acetic acid cooled in ice water, and 8 g. of bromine are run in slowly. After ½ hour, the mixture is poured into water. The 5-bromo-2-acetylamino-*p*-tolyl methyl ether which separates crystallises from alcohol in white needles, m. p. 191° (Found: Br, 30·5. $C_{10}H_{12}O_2NBr$ requires Br, 31·0%).

Hydrolysis of the Bromo-acetyl Compound (III).—The acetyl compound is boiled with strong hydrochloric acid, ammonia added to the clear solution, and the precipitated amine crystallised from alcohol; m. p. 100° (Found: N, 6·45. $C_8H_{10}ONBr$ requires N, 6·5%). By diazotising and coupling with β-naphthol a scarlet azo-dye is obtained which crystallises from benzene in dark red needles having a green lustre; m. p. 210° (Found: N, 7·5. $C_{18}H_{15}O_2N_2Br$ requires N, 7·55%). The benzoyl derivative of the amine made by the Schotten-Baumann reaction melts at 159°.

Conversion of the Amine into 5-Bromoanisic Acid.—Ten g. of the amine with 100 c.c. of concentrated hydrochloric acid are stirred in a freezing mixture while a solution of 3·5 g. of sodium nitrite

is run in; to the resulting solution 20 g. of stannous chloride dissolved in a minimum of hydrochloric acid are added slowly. After ½ hour, the hydrazine hydrochloride which has separated is washed with hydrochloric acid and treated in hot aqueous solution with excess of sodium acetate. The hydrazine forms pale brown needles, m. p. 192°, from alcohol, which darken on exposure to the air.

The hydrazine (10 g. in dilute acetic acid) is run into a boiling solution of copper sulphate (50 g. in 150 c.c.). Ether extracts from the cold reaction product an oil, b. p. 115°/13 mm., which is probably 3-bromo-*p*-tolyl methyl ether (Schall and Dralle, *Ber.*, 1884, **17**, 2531).

Prolonged boiling of the oil with alkaline permanganate solution gives the salt of an acid; the free acid has a melting point, 217—218°, in agreement with that recorded by Schall and Dralle (*loc. cit.*) for 3-bromoanisic acid; but the 2-bromo-acid is recorded by Balbiano, who does not definitely prove its constitution, as melting at 212°. On account of this uncertainty, this acid has been prepared.

2-Bromoanisic Acid.—2-Bromo-*p*-cresol is easily methylated with methyl sulphate and alkali. The resulting oil is extracted with ether and distilled under reduced pressure; b. p. 114°/16 mm. and 222°/760 mm. It is colourless when pure (Found: Br, 40·5. C_8H_9OBr requires Br, 40·0%).

A suspension of the methyl ether is oxidised with alkaline permanganate, manganese removed by adding alcohol, and the hot liquid filtered and acidified. The white solid obtained is crystallised from alcohol and melts at 199° (Found: Br, 34·8. $C_8H_7O_3Br$ requires Br, 34·6%). Mixed with the acid, m. p. 217°, its melting point is 175—185°; this proves satisfactorily the constitution of the former acid.

5-Bromo-2-acetylamino-4-methoxybenzoic Acid.—The bromo-acetyl compound (III) (13 g.) is ground into a fine paste with water, the whole made up to ½ litre, and the correct amount of magnesium sulphate added. Powdered permanganate is added during about 3 hours to the well-stirred mixture at 85°. The liquid is filtered hot, and addition of acid to the cold filtrate throws down a bulky white precipitate. The acid is recrystallised from alcohol and melts at 253° (yield about 70%) (Found: Br, 27·9. $C_{10}H_{10}O_4NBr$ requires Br, 27·8%).

Hydrolysis with Acid.—By boiling the acetylamino-acid with concentrated hydrochloric acid for about ½ hour a clear solution is obtained, which yields a brown solid on the addition of ammonia. This substance crystallises from boiling water in shining plates,

m. p. 90·5°; it shows no acid character, but is soluble in acids and analysis shows that it is a bromo-anisidine (Found: C, 42·0; H, 3·9. C_7H_8ONBr requires C, 41·6; H, 4·0%). In accordance with its method of formation this substance must be *4-bromo-m-anisidine*; its *benzoyl* derivative melts at 124°.

Hydrolysis with Alkali.—Ten g. of the acetylamino-acid, 5 g. of caustic soda, and 300 c.c. of water are boiled together until a test portion gives a precipitate on the addition of acid which is completely soluble in excess of acid (2—3 hours). The hydrolysis mixture is then cooled and acetic acid added in slight excess. The crude *5-bromo-2-amino-4-methoxybenzoic acid* is pale brown and crystallises well from alcohol; m. p. 201°, decomp. 213° (Found: N, 5·7. $C_8H_8O_3NBr$ requires N, 5·7%). The *sodium* salt crystallises in long needles from boiling water (Found: Br, 29·8. $C_8H_7O_3NBrNa$ requires Br, 30·1%). The green *copper* salt is precipitated on adding copper acetate to a faintly acid solution of the anthranilic acid.

5-Bromo-4-methoxy-2-thiolbenzoic Acid.—The amino-acid described above is diazotised by grinding 7·4 g. to a fine paste with 8·7 g. of 30% hydrochloric acid, diluting to 80 c.c., and treating slowly with a solution of 2·1 g. of sodium nitrite, keeping the temperature below 8°. The clear solution is run into a solution of sodium disulphide made from 7·8 g. of $Na_2S,9H_2O$, 1 g. of sulphur, 1·7 g. of caustic soda, and 15 c.c. of water. The mixture is warmed on the water-bath for 1 hour, cooled, and acidified, when di-(bromomethoxythiosalicylic) acid and sulphur are precipitated. The acid is extracted with aqueous sodium carbonate (2 g.) and precipitated by acid.

The acid is boiled in sodium carbonate solution with zinc dust (4 g.) for 3—4 hours, the mixture treated with 1·4 g. of caustic soda, boiled for a short time, filtered, and acidified. On account of the ease with which 5-bromo-4-methoxy-2-thiolbenzoic acid is oxidised it is better to use the solution of its sodium salt directly for the condensation with chloroacetic acid.

4-Bromo-2-carboxy-5-methoxyphenylthiolacetic Acid (IV).—A solution of the sodium salt from 6·6 g. of the thio-acid is heated, with 100 c.c. of water containing 2·5 g. of chloroacetic acid and sufficient caustic soda to form the sodium salt, on a water-bath for 3 hours. The cold reaction product is acidified and the phenylthiolacetic acid, which separates as a pale brown solid, is crystallised from acetic acid; m. p. 243° (decomp.) (Found: C, 37·15; H, 3·1. $C_{10}H_9O_5BrS$ requires C, 37·4; H, 2·8%).

5 : 5′ - Dibromo-6 : 6′ - dimethoxy - 2 : 2′ - bisoxythionaphthen (II).—The finely powdered thiolacetic acid mixed with fused sodium acetate

(1 part) is warmed with acetic anhydride (10 parts) until reaction begins, after which it will continue for a few minutes with great vigour, leaving a clear solution. The excess of acetic anhydride and the acetic acid are removed under reduced pressure and the solid residue is boiled for 10 minutes with excess of 3% alkali. The resulting solution is filtered, cooled, and treated with potassium ferricyanide solution until no more dye is precipitated. The "thioindigo" is dried on the water-bath and crystallised from nitrobenzene, separating in dark red plates, m. p. 355—360° (Found: C, 42·5; H, 2·2. $C_{18}H_{10}O_4S_2Br_2$ requires C, 42·1; H, 2·0%). From its deep blue solution in concentrated sulphuric acid the dye is reprecipitated on dilution with water in a gelatinous state very suitable for preparation of the vat, which is pale yellow and dyes cloth a good scarlet. The solution in nitrobenzene shows an absorption band with a maximum at $\lambda = 529$. "Helindone Fast Scarlet R" shows a similar band with a maximum at $\lambda = 520$.

Condensation of the Thiolacetic Acid with Isatin and with Acenaphthenequinone.—The acid and isatin are boiled together in equimolecular amount with a large excess of acetic anhydride for 3 hours. The mixture gradually turns dark red and, on cooling, the dye (V) separates in small crystals which are washed with alcohol and crystallised from nitrobenzene; m. p. 315° (Found: C, 52·4; H, 2·85. $C_{17}H_{10}O_3NBrS$ requires C, 52·6; H, 2·6%). The dye has a much bluer shade than the "thioindigo" and its solution in sulphuric acid is purple, but its dyeing properties are unsatisfactory, probably on account of further reaction during reduction.

When the thiolacetic acid is boiled in acetic anhydride solution with acenaphthenequinone, an orange powder separates, which is washed with boiling alcohol; m. p. 337°. Its solution in sulphuric acid is dark brown, and it dyes cloth a good orange from a bright blue vat.

We desire to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of us (R. H. G.), and to the Chemical Society for a grant towards the purchase of chemicals.

DYSON PERRINS LABORATORY,
OXFORD.

[*Received, February 13th*, 1925.]

CXXXVI.—*Some Aromatic Chlorovinylarsines.*

By Arthur Frederick Hunt and Eustace Ebenezer Turner.

Acetylene is slowly absorbed by a solution of anhydrous aluminium chloride in phenyldichloroarsine, to give, after treatment with ice and hydrochloric acid, *phenyl-β-chlorovinylchloroarsine*, $AsPhCl{\cdot}CH{:}CHCl$, *phenyl-ββ′-dichlorodivinylarsine*, $AsPh(CH{:}CHCl)_2$, and compounds of higher boiling point. The last, which have not been investigated further, arise mainly from the intermolecular condensation of phenyldichloroarsine, a process which is preceded by the formation of a crystalline *additive* compound, $AsPhCl_2,AlCl_3$.

If the phenyldichloroarsine–aluminium chloride solution is not cooled during the absorption of acetylene, or if the ice–acid treatment is omitted, β-chlorovinyldichloroarsine and benzene are also formed, in accordance with equations of which the simplest is: $AsPhCl{\cdot}CH{:}CHCl + HCl = PhH + AsCl_2{\cdot}CH{:}CHCl$.

Phenyl-ββ′-dichlorodivinylarsine has also been prepared by the action of magnesium phenyl bromide on ββ′-dichlorodivinylchloroarsine.

The reaction between arsenious chloride and phenylacetylene in presence of aluminium chloride is complicated by the polymerisation of the hydrocarbon, and the only isolable product is a yellow, amorphous substance containing two chlorine atoms to each atom of arsenic. Arsenious chloride, however, combines with phenylacetylene in absence of a catalyst, and from the heavy green oil so obtained, *α-chlorostyryldichloroarsine*, $CPhCl{:}CH{\cdot}AsCl_2$, and *αα′-dichlorodistyrylchloroarsine*, $(CPhCl{:}CH)_2AsCl$, have been isolated.

Experimental.

Addition of Phenyldichloroarsine to Acetylene.—Acetylene was allowed to bubble through a well-shaken and cooled solution, prepared in the cold, of anhydrous aluminium chloride in phenyldichloroarsine. Heat was evolved during the absorption and the latter was found to depend to a considerable extent on the proportion of aluminium chloride used. The results of three experiments are given below:

	I.	II.	III.
Phenyldichloroarsine (grams)	61	58	56
Aluminium chloride (grams)	26	17·5	28·5
Acetylene absorbed (grams)	6	4·5	5·2
Time of absorption (hours)	4·5	4	3

The viscous, greenish-brown product was treated with crushed ice, shaken twice with concentrated hydrochloric acid, separated,

dried over anhydrous sodium sulphate, and separated by distillation into two fractions, b. p. 125—220°/15 mm. and 220—270°/15 mm., respectively. The higher fraction could not be separated into its components, and contained about 8% of chlorine attached to arsenic.

The lower fraction was carefully re-fractionated under diminished pressure with a column, when two fractions, *a* and *b*, were finally collected, in addition to a considerable amount of unchanged phenyldichloroarsine.

Fraction a was practically pure *phenyl-β-chlorovinylchloroarsine*, a pale yellow, unpleasant-smelling liquid, b. p. 140—145°/10 mm. (Found: Cl, attached to arsenic, 14·5. $C_8H_7Cl_2As$ requires Cl, 14·3%). This substance, stable when pure, slowly acquires a violet colour if not carefully freed from the last traces of phenyldichloroarsine.

From *Fraction b*, b. p. 150—170°/10 mm., a pure substance could not be obtained by repeated fractionation alone, but when shaken with aqueous silver nitrate, it gave an *additive* compound, $AsPh(CH{:}CHCl)_2,AgNO_3$, white needles, m. p. 142° (decomp.) (Found: Ag, 25·0. Calc., Ag, 24·3%). This was crystallised from water, washed with ether, and decomposed with concentrated hydrochloric acid. The resulting almost colourless oil, after being dried and distilled, was pure *phenyl-ββ′-dichlorodivinylarsine*, b. p. 155—160°/10 mm. [Found: Cl (total), 26·0%; *v. infra*].

This substance, which has a nauseating, fishy odour, was also prepared from ββ′-dichlorodivinylchloroarsine (Green and Price, J., 1921, **119**, 448) (15 g.), which reacted vigorously with magnesium phenyl bromide (20% in excess of that theoretically required) in ethereal solution. The whole was kept gently boiling for ½ hour, and then decomposed and worked up in the usual manner, 14·5 g. of phenyl-ββ′-dichlorodivinylarsine being obtained, b. p. 155—160°/10 mm. [Found: Cl (total), 26·2; As, 27·8. $C_{10}H_9Cl_2As$ requires Cl, 25·6; As, 28·0%]. The silver nitrate additive compound was identical with that described above. Phenyl-ββ′-dichlorodivinylarsine forms crystalline *additive* compounds with chloroplatinic acid and with mercuric chloride, and slowly combines with methyl iodide under pressure at 100° to give a gummy methiodide. In an attempt to prepare 1-phenylarsenopyrrole, the arsine was heated in boiling toluene with metallic sodium. Considerable formation of sodium chloride took place, but the product, which contained 19% of chlorine, was not obtained in quantities sufficient for purification.

During the preliminary work on the addition of phenyldichloroarsine to acetylene, the absorption vessel was in some cases allowed

to become warm. In other experiments, the product was distilled without previous removal of aluminium chloride. In both cases, benzene and β-chlorovinyldichloroarsine (Found: As, 36·5; Cl, 51·3. Calc., As, 36·1; Cl, 51·3%) were isolated, whilst the higher-boiling fractions (above 220°/15 mm.), on standing for some weeks, then decomposed when distilled under diminished pressure, benzene, arsenious chloride, metallic arsenic, and other products being formed.

Action of Aluminium Chloride on Phenyldichloroarsine.—A solution of anhydrous aluminium chloride in cold phenyldichloroarsine (10 parts), on standing for a few hours, deposited the *additive* compound, $AsPhCl_2,AlCl_3$, as pale yellow crystals (Found: Al, 38·3. Calc., Al, 37·5%). If the additive compound, or a freshly-prepared solution of aluminium chloride in the chloroarsine is treated with hydrochloric acid, etc., phenyldichloroarsine is recovered unchanged, but if the solution is kept for more than a few hours, a mixture of products results, the boiling point, ranging from 130° to 270° at 15 mm., being higher the longer the solution stands.

Addition of Arsenious Chloride to Phenylacetylene.—The yellow liquid obtained by mixing phenylacetylene (10 g.), arsenious chloride (40 g.), and anhydrous aluminium chloride (13 g.), when left at the ordinary temperature, became green, then violet, and, after 2 hours, black and viscous. Extraction of the product after the usual acid treatment, followed by precipitation with alcohol, gave a yellow, amorphous solid of indefinite m. p. [Found: As, 5·2; Cl, 4·9%; whence As : Cl (atoms) = 1 : 2]. A similar product was obtained when the addition was carried out at − 20°, or when an excess of arsenious chloride was used.

When phenylacetylene (37 g.) and arsenious chloride (105 g.) were mixed, some heat was evolved; the mixture, after being heated at 110° for 4 hours, became a heavy green oil. The same result was obtained when the original mixture was left at the ordinary temperature for a few weeks. The green oil was shaken with concentrated hydrochloric acid, etc., and distilled under diminished pressure, when two small, but definite, fractions were obtained. These, on redistillation, gave, respectively, (*a*) *α-chlorostyryldichloroarsine*, a fairly mobile, slightly fuming, yellowish-green oil, b. p. 108—110°/12 mm. [Found: Cl (attached to arsenic), 24·4. $C_8H_6Cl_3As$ requires Cl, 25·0%], and (*b*) *αα′-dichlorodistyrylchloroarsine*, an olive-green, viscous liquid, b. p. 170—175°/12 mm. [Found: Cl (attached to arsenic), 9·8. $C_{16}H_{12}Cl_3As$ requires Cl, 9·2%]. Neither arsine possessed an unpleasant odour nor vesicant properties.

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University of London. [*Received, February 11th*, 1925.]

CXXXVII.—*Tesla-luminescence Spectra. Part V. Some Polynuclear Hydrocarbons.*

By William Hamilton McVicker, Joseph Kenneth Marsh, and Alfred Walter Stewart.

In previous papers (J., 1923, **123**, 642, 817, 2147; 1924, **125**, 1743) accounts were given of the spectra emitted under the Tesla discharge by the vapours of benzene and a number of its substitution products. In the present communication the work is extended into the field of polynuclear benzene derivatives and so falls into two parts: first, the spectra of compounds containing two or more isolated benzene rings; and, secondly, the spectra of compounds containing fused rings, such as anthracene and acenaphthene.

The apparatus used is the same as before. The figures given below are wave-lengths. The estimates for the lengths of the various spectra are approximate: the spectra often fade off gradually, and at the red end of the spectrum especially (owing to the small dispersion) it is difficult to determine exactly where the band of light terminates. Other factors involved are the different sensitivity of the photographic plate in various regions and the length of the exposure given. In the results below, the exposure was 15 minutes except where some other period is specially mentioned.

I. *Compounds with Two or More Isolated Benzene Rings.*

1. *Diphenyl*, b. p. 253·8—254·4°/759 mm. A faint continuous spectrum extending from about 2890 to 3900 Å.U., fading off gradually at both ends, with indications of very diffuse bands at 3025 and 3130 Å.U.

2. *Diphenylmethane*, b. p. 261·0—261·8°/745 mm. A medium continuous spectrum running from a fairly distinct head at 2673, to 3900 Å.U. The ultra-violet end of the spectrum is abrupt, whilst the other end fades off gradually. There are indications of very indistinct diffuse heads of bands at about 2736 and 2812 Å.U.

3. *Triphenylmethane*. This substance was obtained pure by a series of recrystallisations from alcohol to remove the by-products of the Friedel–Crafts reaction.

A medium continuous spectrum extending from about 2730 to 4390 Å.U., fading off gradually at both ends, with indications of very diffuse, indistinct heads of bands at about 2820 and 3010 Å.U.

4. *Dibenzyl*, m. p. 53·4°. A faint continuous spectrum running from 2700 to 4300 Å.U. with a brighter region from about 3390 (which is a diffuse head) to 3950 Å.U.

5. *Stilbene*, b. p. 305·0—307·5°/744 mm. A medium continuous spectrum running from about 3100 to 4680 Å.U., and fading off more gradually at the end of greater wave-length. There are no distinguishable bands.

6. *Tolane*, m. p. 60°. A medium continuous spectrum running from about 2915 to 4745 Å.U., fading off more gradually at the end of shorter wave-length. There are no distinguishable bands.

All the above spectra were obtained by an exposure of about 15 minutes on Eclipse plates with the drum-head of the slit at 20. The pressure was 1 mm. or less; and the temperature was sufficiently high to keep the substances vaporised at that pressure.

II. *Compounds containing Fused Rings.*

7. *Fluorene*, m. p. 112°. A very intense continuous spectrum running from 2900 to 4900 Å.U., with a diffuse band-head at 2990 Å.U.

8. *Acenaphthene*. Twice recrystallised from alcohol, this had m. p. 93·5°. Further recrystallisation made no change in the m. p. On visual observation, the discharge in the cell is pink in colour.

A very intense continuous spectrum running from about 2953 to 4650 Å.U., fading off gradually at both ends, with indications of diffuse heads of bands at 3064, 3172, 3207, 3353, and 3523 (?) Å.U. In the visible region, prolonged exposures with panchromatic plates revealed heads of bands at 5540, 5875, 6100, and 6370 Å.U.

9. *Anthracene*, purified by shaking with carbon disulphide, boiling with animal charcoal, and recrystallising; m. p. 216°. An extremely intense spectrum running from about 3240 to 5050 Å.U. with the most intense region between 3650 and 4450 Å.U. Diffuse heads of bands occur at 3247, 3414—44, 3462, 3617, 3642, 3688, 3820, 4055, and 4285 Å.U. The heads are very diffuse, so the foregoing readings are only approximate.

This anthracene spectrum is one of the most brilliant yet observed among the organic compounds. It was tested against an ordinary incandescent mantle at the same distance from the slit; and the two spectra were found to be of approximately the same intensity.

10. *Phenanthrene*, purified by dissolving 3 parts of phenanthrene in 5 parts of warm toluene; then cooling the solution to 10° and filtering to remove anthracene. The filtrate was evaporated until

all the toluene was expelled; and the process was repeated. Finally, the residue was twice recrystallised from alcohol; m. p. 96·2°.

An intense continuous spectrum running from 2960 to 4800 Å.U. the region 2960—3430 being weak and that at 3430—4800 being intense. Heads of bands occur at about 2971, 3430, 3635, 3682, 3819, and 4046. The heads of bands in this spectrum are not so intense as those in the anthracene spectrum.

11. *Naphthanthracene* (1 : 2-*benzanthracene*), m. p. 159°. A continuous spectrum from about 3360 to 4920 Å.U., fading off gradually at both ends and having a very intense region at 3810—4920 Å.U. Diffuse bands occur with heads at approximately 3500, 3635, and 3810 Å.U.

12. 1-*Methylnaphthalene*, b. p. 243·5—244·1°/763 mm. A very intense continuous spectrum running from about 3000 to 4500 Å.U., fading off gradually at both ends, with the most intense region between 3210—4000 Å.U. There are diffuse band-heads at 3115 and 3210, and a less distinct one at 3162 Å.U.

In the visible region, there are diffuse faint bands with heads at about 6020 and 6320 Å.U.

13. 2-*Methylnaphthalene*, m. p. 34°. A very intense continuous spectrum running from about 3000 to 4700, fading off gradually at both ends, with a distinct diffuse head at 3165 and possibly another head of a band at about 3310 Å.U.

There is also a region of emission in the visible, consisting of three bands with heads at (very approximately) 5890, 6030, and 6400 Å.U.

14. 9-*Phenylfluorene*, m. p. 145°, was prepared from triphenylchloromethane by Hemilian's method (*Ber.*, 1878, **11**, 837) and purified by recrystallising three times from glacial acetic acid and finally from alcohol.

An intense continuous spectrum running from about 2900 to 4200, fading off gradually at both ends, with a very indistinct band-head at about 3025 Å.U.

15. 9-*Phenylanthracene*, m. p. 156°.* A very intense continuous spectrum running from about 3550 to 4960 Å.U., fading off at both ends, with very indistinct broad bands of a diffuse character having heads approximately at 3770, 3930, 4155 Å.U.

These five substances—Nos. 11 to 15—gave very good spectra with an exposure of only a few seconds, say 15 seconds, so far as the ultra-violet region is concerned. The visible emission of the two methylnaphthalenes, however, requires an exposure of an hour

* We wish to call attention to this m. p., which is that of a specimen kindly supplied by Mr. E. de Barry Barnett. The m. p. in the literature hitherto has been much lower—152—153°.

with a wide slit in order to produce a clear effect upon panchromatic plates.

16. 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydroanthracene*, m. p. 71·6°. A continuous spectrum of medium intensity extending from about 2835 to about 3800 Å.U., fading off more gradually towards the end of greater wave-lengths, with indications of very diffuse band-heads at about 2835, 2900, and 2940; this last one being the most distinct.

There is also a diffuse band in the green region, with its head at about 4860 Å.U.

To obtain a photograph showing this spectrum of medium intensity, an exposure of 15 minutes was necessary.

17. *Retene*, m. p. 97·5°, was obtained by two recrystallisations with the aid of animal charcoal.

A very intense continuous spectrum running from about 3250 to 4700 Å.U. and fading off gradually at both ends. No bands were detected.

III. *Discussion of the Results.*

(1) *Structural Separation of the Phenyl Groups.*—The influence of substitution on the benzene spectrum may be threefold, since it may affect (*a*) the number of the bands; (*b*) the total extension of the spectrum, and (*c*) the intensity of the spectrum. The following table (Table I) brings out the main changes in the case of the series: benzene, diphenyl, diphenylmethane, and dibenzyl, wherein the phenyl groups are being moved further away from each other in the structure.

TABLE I.

	Emission between.	Bands.	Intensity of spectrum.
Ph·H	2544—3450 (approx.)	78	Bright
Ph·Ph	2890—3900	2	Faint
Ph·CH_2Ph	2673—3900	2	Medium
Ph·CH_2·CH_2Ph	2700—4300	0	Faint between 2700 and 3390 Bright between 3390 and 3950

The approximate extents of the various spectra are thus: Ph·H = 900; Ph·Ph = 1000; Ph·CH_2Ph = 1200; Ph·CH_2·CH_2Ph = 1600 Å.U. The extension is mainly towards the red end of the spectrum, *i.e.*, it progressively includes slower and slower vibrations.

These facts show that the introduction of a second phenyl nucleus in direct attachment to the benzene ring produces a profound disturbance in the original benzenoid vibration; the regularity of the vibration is upset and the amplitude of the vibrations, as measured by the intensity, is reduced. When the second nucleus is separated from the other by a methylene group, the interference is less marked so far as amplitude of vibration is concerned. The diphenylmethane molecule shows no sign of returning to benzenoid regularity of vibration; instead, there is a steady progression of the

emission into the regions of longer wave-length, which suggests either a slowing down of the original vibration or else the production of fresh vibrations by interference.

The accumulation of three phenyl nuclei round a single carbon atom seems to intensify this process; since the triphenylmethane spectrum has a total extension of 1660 units and penetrates farther into the red end of the spectrum than any of the others mentioned above.

(2) *Fused Rings and Independent Nuclei.*—Table II brings into prominence the difference between the spectra of compounds containing two or more complete benzene rings and those of substances in which the six-membered rings have certain members in common, as in naphthalene.

TABLE II.

	Emission region.	Total extent.	Bands.
Diphenyl	2890—3900	1010	2
*Naphthalene	2800—5000	2200	2
Dibenzyl	2700—4300	1600	1
†Acenaphthene	2953—4650	1700	5
Triphenylmethane	2730—4390	1660	2
Anthracene	3240—5050	1810	9
9-Phenylanthracene	3550—4960	1410	3
1 : 2-Benzanthracene	3360—4920	1560	3

* J., 1923, **123**, 1745.

† Acenaphthene has also some bands in the visible region.

The foregoing figures bring out clearly that the fusion of two rings tends to produce a longer spectrum than that produced by the corresponding compound in which the rings have no common members. The intensity of the spectrum is also much greater in the case of the fused-ring compounds than in the analogous substances with independent rings.

Diphenylmethane and fluorene, and triphenylmethane and phenylfluorene might also be cited as examples of this type; but in these substances the ring-fusion produces a fresh cyclic grouping in the molecule. Substances of this nature will be considered in a later paper.

(3) *Conjugated Double Bonds.*—The Tesla-luminescence spectra seem to form an exception to the rule that conjugation has a marked effect upon optical properties. This marks out the Tesla-luminescence rather surprisingly; for the effect of conjugations has been traced in general absorptive power (Crymble, Stewart, Wright, Glendinning, and Rea, J., 1911, **99**, 451, 1262); in selective absorption (Stewart and Baly, J., 1906, **89**, 489); in refractivity (Bruhl, *Ber.*, 1907, **46**, 878, 1153; 1908, **47**, 3712); in magnetic rotation (Sir W. H. Perkin, J., 1906, **89**, 854; 1907, **91**, 806); and in optical rotatory power (Hilditch, J., 1908, **93**, 1388, 1618).

When the intensity of various spectra emitted by compounds containing conjugated chains is examined, the following results emerge.

TABLE III.

	Spectrum.	Bonds directly conjugated.
Diphenyl	Faint	6
Dibenzyl	Faint	3
Naphthalene	Bright	5
Triphenylmethane	Medium	3
Anthracene	Very intense	5
9-Phenylanthracene	Very intense	9
1 : 2-Benzanthracene	Very intense	10

Inspection will show that although in the main an increase in the length of the chain of conjugation seems to enhance the brightness of the spectrum, the first three spectra do not agree with this rule.

An interesting comparison is to be found in the cases of dibenzyl, stilbene, and azobenzene. The absorption spectra of these substances have been described by Crymble, Stewart, and Wright (*Ber.*, 1910, **43**, 1188). The absorption spectrum of dibenzyl contains a series of shallow bands between 3200 and 2400 Å.U. Instead of these, the stilbene spectrum has a single broad and deeply penetrating band covering the same region. The azobenzene spectrum, on the other hand, contains two bands: a broad band in almost the same region as the stilbene band (3450—2550 Å.U.); and a second band of much less penetration in the visible region, 5250—3800 Å.U., which is the origin of the red colour of the compound.

When the Tesla spectra of these three substances are examined, it is found that dibenzyl emits a faint spectrum in the region 2700—4300 Å.U.; stilbene shows an emission of medium intensity in the region 3100—4680 Å.U.; but azobenzene emits no vibrations whatever within the whole region of the photographic spectrum.

The difference between stilbene and dibenzyl might be ascribed to a difference in the length of the chain of conjugation in the molecule, the latter having three double bonds directly conjugated whilst stilbene has seven directly conjugated bonds. But this hypothesis fails to account for the fact that azobenzene with the same number of conjugated bonds as stilbene, and a molecular weight only two units higher, shows no emission whatever. Thus both in absorptive power and in the capacity of Tesla-emission, azobenzene differs from stilbene, although in structure the compounds are extremely similar. It appears that the group –N : N–, like the nitro-group and the chlorine atom, has the power of extinguishing Tesla-emission; and thus the closest resemblances in structure may be overborne by chemical factors.

(4) *Structural Isomerism.*—Both 1- and 2-methylnaphthalene give intense continuous spectra beginning at approximately 3000 Å.U., but whilst the emission of the 1-methyl compound stops at 4500 Å.U., that of the 2-methyl derivative extends up to 4700 Å.U. There is a difference in the positions of the diffuse band-heads in the two spectra also. This shows that even a slight structural difference has its effect upon the nature of the Tesla-spectra.

With deeper alterations in structure, the differences between the spectra of isomerides become more marked, as can be seen from the following figures relating to three compounds with the formula $C_{14}H_{10}$.

TABLE IV.

	Emission.	Region of emission.	Bands.
Tolane	Faint	2915—4745	0
Phenanthrene	Intense	2960—4800	6
Anthracene	Very intense	3240—5050	9

Thus the spectrum is faint when the atoms are grouped in separate nuclei and becomes more intense as the rings are fused into a connected structure. Simultaneously there is a shift of the spectrum towards the red and an increase in the number of bands.

(5) *The Introduction of Substituent Groups.*—Apparently the mode of linking governs the effect of an entering phenyl radical upon the spectra. When the phenyl group is attached to an aliphatic carbon atom, its effect appears to be twofold : it increases the length and diminishes the intensity of the spectrum.

TABLE V.

Aliphatic linking.

	Extent of spectrum.	Intensity.
$Ph{\cdot}CH_3$	2602—3700	Intense spectrum
$Ph{\cdot}CH_2Ph$	2763—3900	Strong medium spectrum
$Ph{\cdot}CHPh_2$	2730—4390	Weak medium spectrum

Similar results are found in the cases of ethylbenzene and dibenzyl; styrene and stilbene; phenylacetylene and tolane.

On the other hand, when a phenyl nucleus is directly attached to *the ring* of a parent compound, the spectrum is shortened and the intensity is, if anything, increased.

TABLE VI.

Phenyl attached directly to ring.

	Extent of spectrum.		Extent of spectrum.
Fluorene	2900—4900	Anthracene	3240—5050
9-Phenylfluorene	2900—4200	9-Phenylanthracene	3550—4960

The introduction of alkyl substituents in the case of fused-ring compounds appears to lead to a shortening of the spectrum, as can be seen from the following figures:

	Extent of spectrum.		Extent of spectrum.
Naphthalene	2800—5000	Naphthalene	2800—5000
1-Methylnaphthalene	3000—4500	Acenaphthene	2953—4650
2-Methylnaphthalene	3000—4700	Phenanthrene	2960—4800
		Retene	3250—4700

IV. *The Sensitiveness of the Tesla Spectra.*

In the course of the present work, an opportunity was accidentally given to test the value of the Tesla-spectra as a means of detecting impurities in the substance under examination. A sample of triphenylmethane obtained through the ordinary trade channels was purified by recrystallisation in the usual manner and was then photographed. Inspection of the photograph showed that the spectrum consisted of two parts: a long faint section beginning about 2700 and merging sharply into a very much brighter band in the region of 3600 Å.U. The position and brilliancy of the latter section suggested that it might arise from a trace of anthracene which still remained in the "triphenylmethane" sample even after ordinary purification. The percentage of anthracene impurity was extremely small, too minute to be detectable by means of the melting point. But by repeated recrystallisation from alcohol the impurity was removed; and the final product gave the true triphenylmethane spectrum, which has no bright band in it at all. Thus the Tesla-spectrum can be used to detect the presence of minute quantities of certain impurities.

It may be mentioned that Baker (J., 1907, **91**, 1494) had a similar experience when examining the absorption spectrum of triphenylmethane. His original sample was contaminated with anthracene, *inter alia*, which is evidently formed as a by-product in the Friedel–Crafts synthesis of triphenylmethane from benzene and chloroform.

In conclusion, we desire to thank the Society for a grant from its Research Fund towards the expenses of this research. We also wish to record our indebtedness to Mr. E. de Barry Barnett for his kindness in supplying us with certain very pure samples of some of the compounds examined.

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NORTHERN IRELAND. [*Received, January 20th*, 1925.]

CXXXVIII.—*The Mechanism of the Formation of Malachite from Basic Cupric Carbonate.*

By JACK REGINALD IRONS HEPBURN.

THIS paper details the results of an investigation into the mode of formation of the crystalline basic cupric carbonate, malachite, from amorphous basic cupric carbonate.

I. *Formation of Malachite in the Cold by Prolonged Keeping.*

Pickering (J., 1909, **95**, 1409) has shown that by intermixture of a cupric salt and a soluble carbonate a voluminous colloidal-amorphous precipitate, having the composition $5CuO,2CO_2$ at the moment of its formation, is produced which, after a few days' contact with the mother-liquor, changes in appearance and colour with production of the stable basic cupric carbonate, malachite ($2CuO,CO_2$).

A series of systematic experiments was made on the influence of dilution and proportion of reagents upon this transformation.

The experiments were carried out with solutions of sodium carbonate and cupric sulphate varying in concentration from saturated to $N/40$. The volume was adjusted in each case so that the amount of precipitate was equivalent to that obtained by intermixture of 25 c.c. of N-reagents. This method follows that of v. Weimarn ("Zustande der Materie," 1914, p. 4) which was employed by him in another connexion.

Preliminary experiments on the initial precipitation with concentrations increasing from $N/200$ showed that within this concentration range the initial precipitate retained the same microscopic form.

The experimental details are summarised in Table I.

TABLE I.

Experiment No.	Strengths of solutions.	C.c. of Na_2CO_3.	C.c. of $CuSO_4$.	Malachite formed after (days).	Experiment No.	Strengths of solutions.	C.c. of Na_2CO_3.	C.c. of $CuSO_4$.	Malachite formed after (days).
I	$N/40$	1000	1000	18	VII	$N/2$	50	50	3
II	$N/40$	1400	1000	13	VIII	$N/2$	80	50	7
III	$N/20$	500	500	10	IX	N	25	25	2
IV	$N/20$	800	500	9	X	N	40	25	6
V	$N/10$	250	250	4	XI	$N/10$	250	250	30
VI	$N/10$	400	250	8				+ 5 c.c. of 20% gelatin.	

The times given are approximate only, and indicate periods after which the microscopic appearance showed no further change.

In Expt. V the initial products of the precipitation were the basic carbonate, sodium sulphate, and carbonic acid. When the

precipitate from $N/10$-solution was washed free from all adhering reagents and suspended in water free from carbon dioxide, the transformation was completely inhibited. But the change to malachite was accomplished when the well-washed colloidal precipitate was suspended in an aqueous solution of carbon dioxide.

In Expt. VI the initial products of the precipitation were the basic carbonate, sodium sulphate, and sodium hydrogen carbonate. The metamorphosis in this case was brought about through the agency of the sodium hydrogen carbonate, a fact which was demonstrated directly by the occurrence of the same change on suspending the well-washed basic carbonate in sodium hydrogen carbonate solution of the same concentration.

Experiment XI consisted in the repetition of Experiment V in the presence of 0·2% of gelatin. The change was considerably retarded, but was otherwise unaltered, malachite again being the final product. Mond and Heberlein's statement (J., 1919, **105**, 908) that a small amount of gelatin (0·1%) stabilised the precipitate, does not appear to be confirmed by this result.

When the basic carbonate was suspended in $N/10$-sodium carbonate solution, blackening ensued after 3 days with loss of carbon dioxide and formation of sodium hydrogen carbonate. A similar result was obtained by Pickering (*loc. cit.*), both results being contrary to Mond and Heberlein's statement (*loc. cit.*) that in the presence of sodium carbonate solution the amorphous precipitate was stable.

The course of the change in every case above was followed by microscopic observations.

Freshly precipitated basic cupric carbonate (over a range of concentration from $N/200$ to $3N$) consisted of a hydrogel and appeared under the microscope as ill-defined aggregates of gelatinous highly-hydrated material of low refractive index, and absolutely opaque in polarised light.

Sharply-defined changes of a similar nature were observed in all concentrations lower than $N/10$, after allowing the precipitate to stand. With the stronger solutions the changes were not so well marked. The formation of malachite with $N/10$-reagents (Expt. V) was of especial interest. After 4 days' standing, a drop of liquid containing the product in suspension was examined under the microscope. The product was evidently crystalline and consisted of green and blue sphærocrystals ($d = 100\mu$). After 10 days' standing, a further profound change had occurred, with production of sharp excrescences over the surface of each sphærocrystal. The final product consisted of normal malachite crystals which reacted brilliantly in polarised light (Fig. 1. × 240).

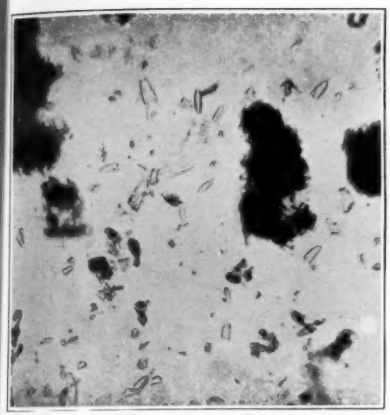


FIG. 1.—*Normal malachite* (×240).

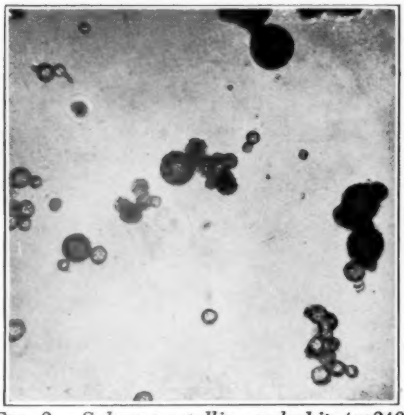


FIG. 2.—*Sphærocrystalline malachite* (×240).

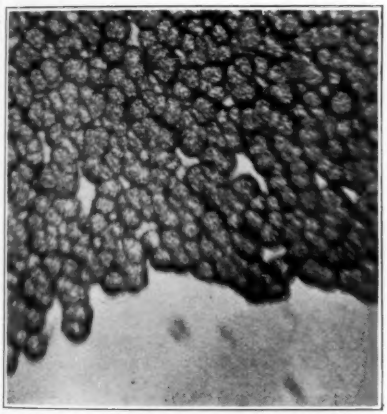


FIG. 3.—*Film of malachite* (×240).

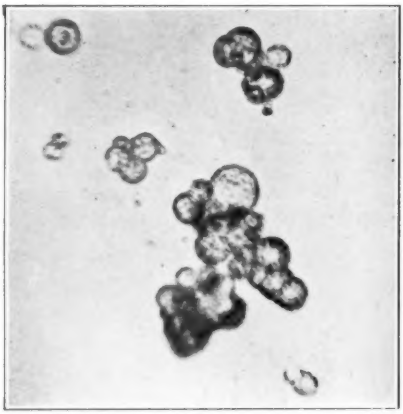


FIG. 4.—*Sphærocrystalline malachite* (×480).

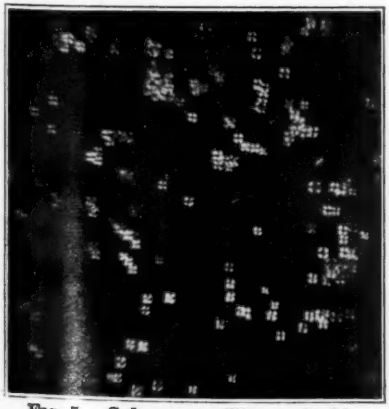


FIG. 5.—*Sphærocrystalline malachite* (*polarised light*) (×240).

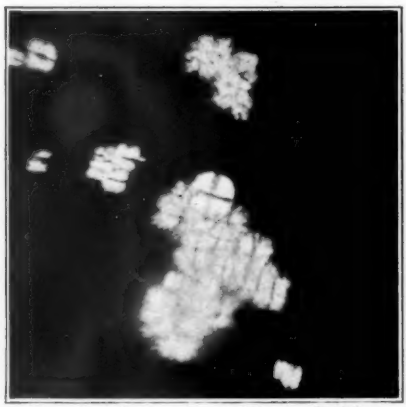


FIG. 6.—*Sphærocrystalline malachite* (*polarised light*) (×480).

[*To face p.* 1008.

In Experiment VI, after 6 days' standing, microscopic examination revealed the presence of minute spheres embedded in the gelatinous masses. Regular growth continued within the hydrogel, and the final product presented the appearance shown in Fig. 2 (× 240) and consisted of malachite sphærocrystals, some of great structural beauty, and reacting normally to polarised light.

Similar, but less rapid changes occurred with the more dilute reagents. With *N*-reagents, the sphærocrystals were very much smaller in size, imperfect in formation, and aggregated.

II. *Formation of Malachite from Hot Solutions.*

A modification of Field's method was used (J., 1862, **14**, 70).

Saturated cupric sulphate solution was added from a burette to 50 c.c. of a freshly-prepared saturated solution of sodium hydrogen carbonate with violent agitation, in the cold, until the precipitate no longer redissolved. A further equal volume of cupric sulphate was added, and the whole rapidly heated at 100°. After a few minutes, the deep blue solution suddenly decolorised, and a green, lustrous film, consisting of malachite, formed on the walls of the vessel. The film was readily detached and disintegrated by further boiling.

In the presence of the normal carbonate, malachite was not precipitated at 100°, but a black powder containing less carbonic acid was formed as a similar film. A similar effect was observed if the sodium hydrogen carbonate solution was not freshly prepared. This action was subsequently shown to be due to the presence of the normal carbonate.

If the basic carbonate initially precipitated remained partially undissolved on heating at 100°, it was converted directly into malachite without intermediate film formation.

In the presence of 0·5% of gelatin, the blue solution gave the same products; the reaction, however, was greatly retarded, and occupied 30 minutes instead of from 2 to 3 minutes.

Microscopic observation showed the film of malachite to consist of what may be termed colonies of embryo sphærocrystals (Fig. 3. × 240). The individual sphærocrystals were very uniform in size, and the film reacted to polarised light. After the solution had been boiled for a short time, the film disintegrated into individual sphærocrystals and larger aggregates. Many of the larger spheres showed well-marked zonal structure. When formed without intermediate film formation (Fig. 4. × 480), the malachite consisted of small and poorly developed sphærocrystals, generally aggregated in clusters.

Some light may be thrown on the cause of the origin of sphærocrystals by the following considerations. Applebey and Lane (J.,

1918, **114**, 609) have suggested that the blue solution contains a suspensoid (basic cupric carbonate or a double sodium cupric carbonate); the evidence brought forward in support of this assumption, however, seems somewhat inadequate, and appears to rest on the observation that addition of a large amount of sodium phosphate precipitated the blue salt. Further evidence in favour of the view that a suspensoid is present in the blue solution is found in the fact that such solutions show a well-marked Tyndall cone in which the light scattered at right angles to the entrant beam is plane polarised. The assumption of the presence of a suspensoid is in accordance with the intense colour of these solutions (compare Applebey and Lane, *loc. cit.*, p. 620); further, Bradford (*Biochem. J.*, 1918, **12**, 357) has suggested—in another connexion—that sphærocrystals are the products of coagulation of aggregated particles of colloid dimensions. Hence it seems possible that malachite sphærocrystals may be produced, with intermediate film formation, through coagulation of the colloid by heat. In this case the function of gelatin in retarding this change would be that of a normal protective colloid and would be analogous to its action in stabilising solutions of colloidal gold.

Morphological and Optical Properties of Malachite Sphærocrystals.

Following the method described above, malachite may be prepared in quantity in the form of sphærocrystals of uniform size.

Size of Particles.—This was determined by two independent methods.

I. *By the scale micrometer.* A scale micrometer standardised against a Zeiss stage micrometer (graduated to 1/100 mm.) was employed, with $\frac{1}{6}$-inch objective. From several observations the mean diameter was found to be 6 μ.

II. *By halo production.* A similar method for the average diameter of a group of particles of uniform size has been employed by Young (*Ann. Philos.*, 1813, **2**, 115) and elaborated by Quincke (*Ann. Physik*, 1902, **7**, 734).

The source of illumination employed was a single straight-filament carbon lamp, which was viewed through the malachite slide together with a green glass, in the first experiment, and a red glass in the second. The prominent wave-length of the light transmitted was determined from observations with the spectrometer (for green glass = 0·00053 mm.; red glass = 0·00064 mm.).

From the width (b cm.) of the halo the diameter of the particles (d mm.) was calculated according to the formula

$$d = \lambda E b,$$

where λ = wave-length of light used (mm.) and E = distance between the source of illumination and the slide (cm.).

For green light b was found to be 14 cm., and for red light, 17 cm. Each of these values gives $d = 6\mu$.

The result is in agreement with that obtained by direct microscopic observation. This method seems well adapted for the determination of the average diameter of particles of uniform size.

Density.—It has been suggested that sphærocrystals are closely allied in nature to colloid substances under strain (Quincke, *loc. cit.*; Bradford, *loc. cit.*), in which case the density of the sphærocrystalline modification of a substance would probably differ from that of the normal crystalline form. The suggestions above were put to the test by determinations of the density of sphærocrystalline malachite. Using the specific gravity bottle, the result obtained was 3·64 (mean of two concordant determinations).

This result is slightly lower than that for natural malachite (d 3·7 to 4·0). However, it would not appear justifiable to draw definite conclusions from such small variations.

The value obtained above was confirmed by observations of the rate of fall of the particles in a cloud. A suspension of malachite was prepared in air-free distilled water, and allowed to subside in a tube of small cross-section.

The rate of fall (v) was $4{\cdot}3 \times 10^{-3}$ cm. per sec., which gave a value of 3·6 for the density, d, as calculated from the ordinary formula

$$d - D = 9\eta v/2r^2g,$$

where D is the density of water and the other letters have the usual significance.

The difference in the density of individual sphærocrystals was also investigated by observation of the rate of transit across the microscopic field, using a $\frac{1}{4}$-inch objective and capillary tube.

The apparent diameter of the field was 3·50 mm. The variation in the times of transit of individual particles was small and the average time of transit, 77 seconds. From the average observation, the density was found to be 3·7.

Optical Properties.—The sphærocrystals of malachite, when viewed with crossed nicol prisms, showed a characteristic interference pattern, photographs of which are shown in Figs. 5 (× 240) and 6 (× 480). The pattern consisted of a dark cross with four bright sectors, surrounded under certain conditions by colour rings. The same reaction is shown by circular particles of amorphous substances under strain. This provides a means of testing the assumption of crystallinity in the malachite spherites. Spherites of amorphous substances under strain, together with those of uniaxial

crystalline substances (*i.e.* belonging to the tetragonal, hexagonal or orthorhombic system) exhibit a shadow cross with the arms accurately at right angles (Rosenbusch, *Mikroscopische Physiographie*, 1904, **1**, 395). The pattern observed is identical with that produced by convergent polarised light impinging upon a thin plate of a uniaxial crystal (compare Tutton, "Crystallography," 1911, p. 670). Spherites of biaxial crystalline substances (*i.e.*, belonging to the monoclinic or triclinic system), on the other hand, show shadow crosses, the arms of which are not accurately at right angles, the pattern produced being closely analogous to that shown by biaxial crystalline plates in convergent polarised light. An examination of Figs. 5 and 6 reveals that the pattern shown is a biaxial one, certain particles exhibiting the characteristic design seen on rotating a biaxial crystalline plate in convergent polarised light. They are clearly not amorphous substances under strain. This observation is in agreement with the fact that naturally occurring normal malachite crystals are optically biaxial and belong to the monoclinic system (Dana, "Mineralogy," 1899, p. 295).

Summary.

The course of the changes which occur in the transformation of the unstable amorphous cupric carbonate into the stable crystalline substance, malachite, has been followed by direct microscopic observation throughout a wide range of concentrations, at the ordinary temperature and at 100°.

Transformation in the cold appears to be brought about through the intermediate agency of an aqueous solution of carbon dioxide or sodium hydrogen carbonate. In the presence of a solution of carbon dioxide, the resulting malachite consists of normal crystals. When the change is brought about by sodium hydrogen carbonate, the product consists entirely of malachite sphærocrystals. These are probably produced through crystal growth in a colloid medium (*viz.*, the unchanged basic cupric carbonate). In the presence of gelatin the change is considerably retarded, but is unaltered both in character and in products. When malachite is formed at 100° by thermal decomposition of the blue solutions prepared by dissolving the basic carbonate in saturated sodium hydrogen carbonate solution, the product (in the absence of foreign nuclei) consists of a surface film of interpenetrating sphærocrystals. The film is disrupted into individual sphærocrystals by further boiling. The direct cause of the change is to be attributed to loss of carbon dioxide from the sodium hydrogen carbonate at 100° with formation of the stable double salt $Na_2CO_3,NaHCO_3,2H_2O$ (Habermann and Kurtenacki, *Z. anorg. Chem.*, 1909, **63**, 65) and malachite.

Gelatin similarly retards this change.

As far as a search of the literature has been made, this records one of the first cases in which sphærocrystals form the sole product of a normal chemical reaction.

The author wishes to express his thanks to Dr. T. J. Drakeley for the interest he has taken in this investigation.

NORTHERN POLYTECHNIC INSTITUTE,
LONDON, N. 7. [*Received, February* 14*th*, 1925.]

CXXXIX.—*Periodic Electrochemical Phenomena.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

IN continuation of the work being developed in this laboratory on the principle of periodicity in chemistry, some of the periodic reactions previously described (J., 1924, **125**, 604, 1282; this vol., p. 445) have been examined from the electrochemical standpoint. This method not only furnishes a delicate means of following the course of reactions where the rate of evolution of gas is so slow as to render the manometric method inapplicable, but also provides data which are of importance in the elucidation of the mechanism involved in the periodic dissolution of metals. Further, it would seem that the method has a considerably wider scope, being adapted in particular to the case of reactions involving the deposition of metals, and it is intended to continue investigations in this direction.

There are scattered throughout the literature several reported cases of periodic electrochemical phenomena, and as consideration of these is important not only in their bearing on the work described here, but is also essential to the correct presentation of periodicity as a principle, a brief account is given of the results of previous investigators. The work may be considered in two sections: (*a*) where current is taken from the system, (*b*) where current is led into the system.

Section (*a*).—Early cases of such periodicity concerning an iron electrode are mentioned by Fechner (*Schweigg. Journ.*, 1828, **53**, 141) and by Schönbein (*Pogg. Ann.*, 1836, **38**, 444). Kistiakowsky ("Nernst-Festschrift, Knapps Verlag.," Halle-a-S., 1912) obtained a periodic current from the cell—Fe(rusted)|5% $K_2Cr_2O_7$,*N*-H_2SO_4|Fe (periodic)—in which the electrode responsible for the periodicity consisted of the purest iron, scrupulously cleaned and then immersed in 10% sulphuric acid before the experiment. By employing two electrodes of similarly treated iron in the same solution, he suc-

ceeded in making a cell which produced an alternating current—the two electrodes periodically reversing in polarity (*Z. Elektrochem.*, 1909, **15**, 268). It is interesting to observe that in this case the metal requires a quite definite form of treatment or activation. Kistiakovski also found (7th Intern. Congr. Appl. Chem., 1909, Sect. 10, 56) that iron becomes alternately active and passive in dilute nitric acid, chromic acid, or potassium permanganate solution.

Brauer (*Z. physikal. Chem.*, 1901, **38**, 441) obtained a fluctuating difference of potential between Ostwald's chromium and the solution in which it dissolved, and Antropoff (*ibid.*, 1908, **62**, 513) found the potential difference between mercury and hydrogen peroxide to vary periodically, synchronising with the periodic evolution of gas. Heyrovský (J., 1920, **117**, 28) describes sudden changes and fluctuations between the values 0·77 and 1·67 volts for the E.M.F. of the cell $Hg|Hg_2Cl_2,N\text{-}KCl|Al$. This is precisely similar to the periodic dissolution of aluminium amalgam in hydrochloric acid described by the present authors (*loc. cit.*, p. 622).

Section (*b*).—Periodic fluctuations in current were observed by Schönbein (*Archives de l'Electricité*, 1842, **2**, 269) in leading a current through the cell $\overset{+}{Fe}|dil.H_2SO_4|\overset{-}{Pt}$, and by Joule (*Phil. Mag.*, 1844, **24**, 106) when a potential difference of 3·3 volts was applied to the cell $\overset{+}{Fe}|H_2SO_4|\overset{-}{Zn}$ amalgam. There were corresponding periods of dissolution of iron and evolution of oxygen at the anode. Heathcote (*Z. physikal. Chem.*, 1901, **37**, 368) states that when a current was passed through the cell $\overset{-}{Pt}|HNO_3(d\ 1{\cdot}4)|\overset{+}{Fe}$, the needle of an ammeter placed in series exhibited regular oscillations. Different results were obtained with different pieces of iron and it may be observed that in many of these cases the influence of minute traces of impurities is not excluded, and the effect may be due—as in Ostwald's experiment with chromium—to an activating agent already present in the metal. Fredenhagen (*Z. physikal. Chem.*, 1903, **43**, 1) electrolysed sulphuric acid with an iron anode and obtained a periodic current after addition of chlorine ions. This result may be compared with the experiments of the present authors (experimental portion of this paper) on the deposition of iron on magnesium from solutions in sulphuric acid (non-periodic) and hydrochloric acid (periodic).

Adler (*Z. physikal. Chem.*, 1912, **80**, 385) extended Joule's experiments on the periodic electrolytic dissolution of iron and studied the effect of varying current density and other conditions of experiment. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 807; *Versl. Kon. Akad. Wetensch. Amsterdam*, 1915, **24**, 745;

1918, **27**, 159) found that with certain current densities an iron electrode immersed in a solution containing a mixture of ferrous sulphate and ferrous chloride gave a potential rapidly alternating from a positive to a negative value with an amplitude of 1·74 volts. He explains this as due to the periodic acceleration of establishment of inner equilibrium in the metal by the chlorine ions, but admits that this cannot explain Adler's results.

Another instance of periodic electrolytic phenomena occurring at the anode is given by Müller (*Z. Elektrochem.*, 1904, **10**, 519), who observed pulsations in the E.M.F. of a manganese electrode dissolving in faintly acid sodium phosphate solution. Byers observed a similar effect (*J. Amer. Chem. Soc.*, 1908, **30**, 1729), using a cobalt anode in sodium sulphate solution. Liebreich (*Z. Elektrochem.*, 1921, **27**, 94; compare also Kleffner, *ibid.*, 1923, **29**, 448) describes periodic phenomena in the electrolysis of chromic acid. Kohlrausch reports (*Physikal. Z.*, 1900, **1**, 88) that, when electrolysing platinum tetrachloride for the purpose of preparing pure platinum, he had once obtained a periodic evolution of gas, but subsequent attempts to repeat this had proved unsuccessful.

Periodic changes in anodic potential and in current density were observed by Küster (*Z. anorg. Chem.*, 1905, **46**, 113) and by Köhlichen (*Z. Elektrochem.*, 1901, **7**, 629) during the electrolysis of sodium sulphide solution with platinum electrodes. There was a corresponding periodic formation and dissolution of a film of sulphur over the anode surface. The chief factors in the production of waves were found to be the *size, position, and nature of surface* of the platinum electrodes. In general, the phenomenon did not occur at all when bright platinum foil was used, and a rough surface was found to answer best. These facts find a ready explanation in the light of the experiments of the present authors concerning the activation of metals. In all probability, the periods were only obtained when the platinum was in the active state. Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1291) observed a similar periodicity in the electrolysis of alkali iodides between platinum electrodes. Examples are given of irregular waves resembling those often obtained by the present writers when the activating agent has been a metal. Windelschmidt (*Diss.*, Münster, 1907) and Dietrich (*Diss.*, Münster, 1910) obtained a periodic current in the electrolysis of ammoniacal solutions of nickel salts.

Several cases are also on record of periodic electrochemical phenomena occurring at the cathode. Förster (*Z. Elektrochem.*, 1902, **8**, 500) found the deposition of copper from a strongly acid solution of the nitrate to be periodic at high current densities, and a similar case is quoted by Cohen (*ibid.*, p. 499) in electro-

lysing an acid solution of bismuth nitrate. Kremann and Suchy (*Wiener Sitz.*, April, 1913) found a periodically changing cathode potential in the deposition of a 50% iron–nickel alloy from a mixture of the sulphates. Coehn (*Z. Elektrochem.*, 1901, **7**, 633) electrolysed a solution of an alkali salt with a mercury cathode and noticed that the surface of the mercury alternately became grey and then bright, whilst hydrogen was evolved during the bright periods. The course of the phenomenon was registered photographically by Kremann and Lorbeer (*Wiener Sitz.*, April, 1913). Mercury is the one metal which the present authors believe to be normally periodically active. Haber (*Z. Elektrochem.*, 1901, **7**, 634) observed periods in the electrolytic reduction of nitrobenzene in alcoholic solution at a platinum cathode.

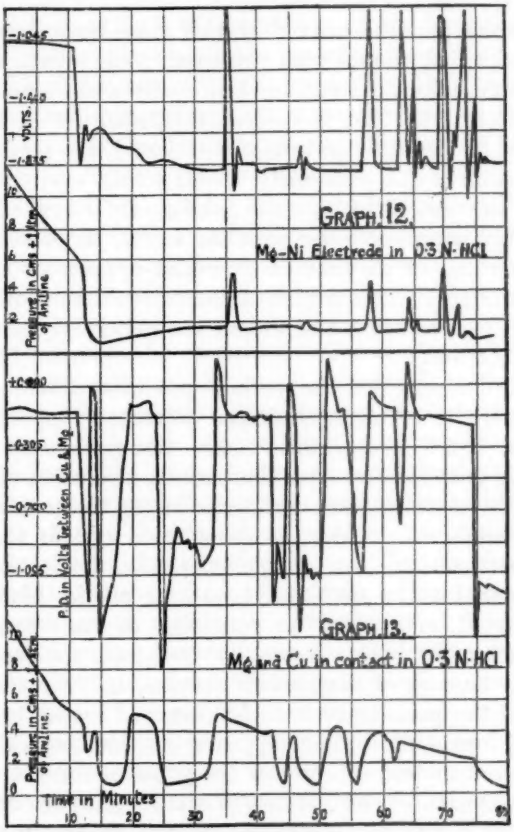
It is relevant to mention the pulsations of the mercury surface observed by Roshdestwensky and Lewis (*Trans. Faraday Soc.*, 1912, **8**, 220) when mercuric cyanide was used in a capillary electrometer.

Experimental.

The Apparatus.—The measurements of potential were made with a Dolezalek quadrant electrometer, the needle of which was charged to 90 volts by means of a battery of dry cells. The system consisted of one or more metal electrodes immersed in the appropriate solution contained in a glass bottle of 100 c.c. capacity, which was fitted with a wide rubber stopper carrying glass tubes through which the electrodes were sealed. The reading scale was so placed that one volt gave a deflection of 273 divisions (mm.). By means of a bridge of saturated potassium chloride solution leading to an auxiliary saturated calomel electrode, it was possible to determine the potential difference between the two metal electrodes immersed in the solution or between each metal and the standard reference electrode. In either case, one electrode was earthed and the other connected to one pair of quadrants of the electrometer, the other pair also being earthed. The method of suspension of the metal electrodes was found to be of importance and in the first experiments, where the metals were suspended from platinum hooks sealed into glass tubes, constant results were not always obtained. The difficulty was overcome by fastening the metals to a stout platinum rod with the aid of a platinum screw. The rod was soldered to copper wire and sealed into glass by means of wax.

In later experiments, in order to compare the chemical and electrical effects, the apparatus was combined with that described by the authors in a previous paper (*loc. cit.*), the course of the reactions being recorded simultaneously on the electrometer scale and on the manometer. The two sets of curves agree very closely

when the frequency and amplitude of the oscillations are not great, but in order to register the short waves electrically it would be necesary to use a more dead-beat instrument. The natural period of the electrometer needle suspended as in these experiments was 16 seconds. Simultaneous readings of potential and of gas pressure were taken every 30 seconds and the potentials recorded



are expressed with reference to the saturated calomel electrode. All the experiments were carried out at room temperature.

Examination of some Metal Systems.

The authors have already shown (*loc. cit.*) that certain metallic couples dissolve in acids in a periodic manner after the second metallic component (*i.e.*, the cathodic metal which does not dissolve) has been treated or "activated" by certain processes. Graph 12 represents the potential against the saturated calomel

electrode acquired by such a couple of magnesium and nickel sheet dissolving in 0·3*N*-hydrochloric acid, and below is plotted the synchronous variation in gas pressure. The periods are not very regular, but this is often a feature of systems where the activating agent is a second metallic component, and in a former communication (this vol., p. 445) a study was made of the conditions necessary to ensure regularity of wave form.

Simultaneous periodic curves of this type have been obtained with couples of magnesium with platinum, gold, cobalt, and copper in ammonium chloride solution, and with aluminium amalgam in hydrochloric acid. In the example illustrated in the graph, and in many of the other instances mentioned, the periodic nature of the evolution of gas was easily visible to the eye. It appeared that during the periods of high gas pressure the excess of hydrogen came from the nickel or other cathodic metal, the dissolving magnesium preserving at all times a slow and apparently steady rate of evolution of gas. This is quite in accordance with other experiments which indicate that the seat of the periodicity is the second metallic component.

In Graph 13 is recorded the periodic potential difference existing between electrodes of magnesium and activated copper in contact immersed in 0·03*N*-hydrochloric acid. Comparison of this with the foregoing graph shows that the periodic evolution of hydrogen is attended by simultaneous variations in (*a*) the potential of the couple as a whole with respect to the solution and (*b*) the potential difference between the two components. In the latter case, the copper appeared to be quite inert so long as the high potential difference lasted, and when the potentials of the two metals approached each other hydrogen was evolved from the surface of the copper. In the case of magnesium couples, another easily visible indication of the periodicity is to be observed in the behaviour of a dark grey oxide film which appears on the magnesium. This film forms even in acid solution at the point of contact of the two metals and extends for the distance of a millimetre or two. During the periods of strong gas evolution, the film begins to spread and may grow to a length of 1 or 2 cm. When the next slow rate of evolution commences, the film dissolves gradually, but not completely. The formation or dissolution of this oxide film has been observed always to follow and never to precede the change in potential of the couple. The authors therefore regard its appearance as a concomitant effect of the inherent periodicity rather than as a cause of the phenomenon, as in the case of the periodic mercury-hydrogen peroxide catalysis (*loc. cit.*, p. 1283).

Periods have not been obtained, in experiments with platinum,

gold, silver, and nickel as activating agents, when the cathodic and dissolving metals were not in contact. Some contradictory results obtained, with copper, were probably due to the slow dissolution of this metal, which is known to take place in hydrochloric acid, followed by reduction at the surface of the magnesium.

Effect of Activation on the Potential of Metals.

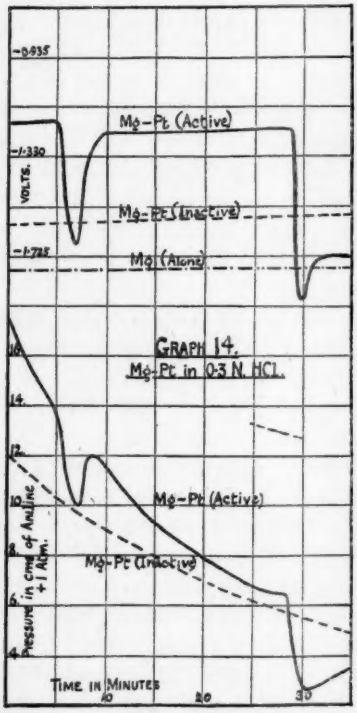
It is well known that the condition of the surface of a metal has a considerable influence on the potential it acquires, and experiments by Vieweg (*Ann. Physik*, 1924, **74**, 146) show that the contact potentials, measured against a standard metal, of aluminium, copper, nickel, gold, and platinum are affected by heating in a vacuum in a similar way to the change produced by mechanical cleaning of the surface. It has now been found that the value for the metal after treatment differs considerably from that of the inactive metal. The change is in the negative direction in the cases of copper and silver, and positive in the case of platinum and of gold. The potential of ordinary copper foil in 0·3*N*-hydrochloric acid against the saturated calomel electrode was determined as — 0·11 volt and the values — 0·26, — 0·19, — 0·22 volt were obtained with different specimens of the active metal after scraping. A sample of copper after vacuum-heat treatment registered a potential of — 0·18 volt. A silver electrode after vacuum-heat treatment changed its potential in *N*-hydrochloric acid by 0·03 volt in the negative direction. Gold in 0·1*N*-hydrochloric acid gave an initial value of + 0·17 volt, changing, after vacuum-heat treatment, to + 0·25 volt. Platinum (platinised) in *N*-hydrochloric acid registered a potential of + 0·19 volt, which became + 0·38 volt after treatment. The difference is not so great as that brought about by depositing platinum black on a platinum surface. The potential of a piece of bright platinum foil in 0·1*N*-hydrochloric acid was + 0·19 volt, and this became + 0·48 volt after platinising from a solution of chloroplatinic acid. After keeping for 3 days, this high value sank to + 0·41 volt. The potentials of activated metals gradually return to the normal value on keeping, corresponding with the previously described dying of the activity.

Another factor entering into the consideration of the potentials assumed by activated metals during the reactions is the influence of the hydrogen with which the solution soon becomes saturated and which is absorbed by the metal. The effect of this is to make the metal more negative, but on standing for an hour there is a partial return to the former value. In the case of activated copper, the effect due to the hydrogen is complicated by the partial return

of the metal to the inactive state—a factor operating in the reverse direction. Graph 14 conveys a clear impression of how the dissolution of magnesium in 0·3*N*-hydrochloric acid is affected by contact with activated and with inactive platinum, both from the electrical and from the chemical point of view.

Some Reactions involving the Deposition of Metals.

When magnesium dissolves in dilute hydrochloric acid containing ferrous sulphate in solution, reduction takes place and iron is deposited as a black film on the surface of the magnesium. By suitably choosing the concentration of the reagents, periodic phenomena may be observed in this reaction. This particular case was first found by the visible periodic changes which occur in the system; in fact, the system itself serves admirably as an optical demonstration of chemical periodicity. After an initial lapse of time dependent on the relative concentrations of the reagents, a film of reduced metal spreads from one or two centres on the magnesium surface until it covers about half the metal electrode. Then it proceeds to dissolve, leaving the electrode with a bright surface. The black film grows a second time, covering a greater surface of electrode, and then redissolves, leaving a few black patches on the magnesium. These two processes continue in alternation a number of times and in each successive period both the area covered by the growing film and the area of the film remaining after the partial dissolution increase. This continues until finally the film, even in its partially dissolved state, entirely covers the electrode. There is no reason to suppose that the periodic phenomenon is then at an end. It is probable that the film continues to grow periodically in thickness as it can no longer do so in extent, and when the surface is once complete no further change in the potential is to be expected. Hydrogen is evolved throughout.



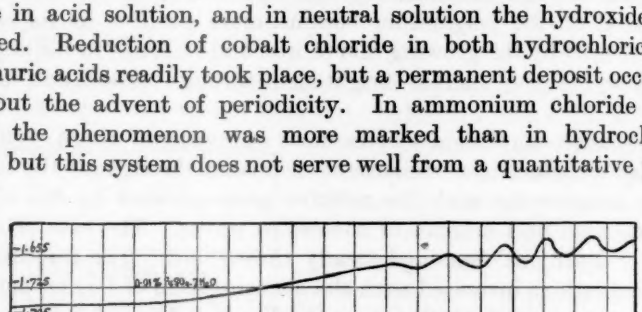
The change has been followed in the apparatus described, simultaneous observations being made of the potential of the dissolving metal, the pressure of the evolved hydrogen, and the appearance of the film. The electrical change synchronised exactly with the chemical change indicated by the appearance of the film. The potential of the magnesium became more positive as its surface was covered by the growing film of iron and returned in the negative direction as the surface brightened through dissolution of the film.

The mean amplitude was in most experiments about 0·03 volt. The amplitude of the oscillations decreased throughout the experiment consistently with the relative areas covered by the film at the maxima and minima of successive waves. The rate of evolution of hydrogen remained steady throughout. The frequency of the oscillations increased with the concentration of ferrous sulphate and was independent (between the limits 0·6*N* and 0·2*N*) of the concentration of acid. The authors have found (*loc. cit.*, 1924, p. 611; this vol., p. 447) that the frequency of other periodic reactions is proportional to the concentration of reagent and *decreases* with increasing amount of activating agent. The hydrochloric acid and the ferrous sulphate are not to be regarded, therefore, as reagent and activating agent respectively, but rather the ferrous sulphate is the reagent and the reduced iron is an active second metallic component. This is also consistent with the absence of periodicity in the rate of evolution of hydrogen. Experiments in which the solution was vigorously stirred by means of an air blast showed that the phenomena were not affected thereby in any way. This removes any possibility of a periodic diffusion of the reactants or reaction products.

Graph 15 represents some of the experiments which have been carried out on this system, and shows the effect of varying the concentration of ferrous sulphate between the limits 0·01% and 0·05% of $FeSO_4,7H_2O$, the hydrochloric acid being kept at 0·3*N* strength. In these curves, the first reading was taken 3 minutes after the commencement of the experiment, in order to eliminate the initial vigorous swinging of the electrometer needle. In an experiment in 0·3*N*-hydrochloric acid with addition of 0·1% of crystallised ferrous sulphate, the periodic film formation was observed during the first 3 minutes, after which the permanent deposit set in, so that electrical measurements could not be taken. It is probable that in stronger solutions, where the deposition takes place immediately on immersing the metal, very rapid oscillations incapable at present of detection are actually existent.

When the hydrochloric acid was replaced by 0·3*N*-sulphuric

acid, no periodicity was observed, the reduced iron gradually forming a permanent deposit. Experiments have also been conducted in hydrochloric acid in which the ferrous sulphate has been replaced by an equivalent quantity of nickel chloride or cobalt chloride. In the case of nickel chloride, reduction did not take place in acid solution, and in neutral solution the hydroxide was formed. Reduction of cobalt chloride in both hydrochloric and sulphuric acids readily took place, but a permanent deposit occurred without the advent of periodicity. In ammonium chloride solution, the phenomenon was more marked than in hydrochloric acid, but this system does not serve well from a quantitative point



of view, since the solution quickly becomes alkaline with ammonia and reacts with the metal salt. Periodic phenomena similar to those described above have been observed with magnesium dissolving in 2% ammonium chloride solution with addition of 0·001% of crystallised cobalt chloride, 0·05% of crystallised ferrous sulphate, 0·001% of crystallised nickel chloride, or 0·002% of crystallised copper sulphate. The smallness of the quantities involved is characteristic of the conditions underlying periodic chemical action. In all these instances, the rate of evolution of hydrogen was also periodic. This may be a secondary effect, for it has been shown by the authors (this vol , p. 495) that couples of magnesium with these metals reduced in ammonium chloride solution are very active, decomposing water at the ordinary temperature. It is to be expected, therefore, that the rate of evolution of hydrogen would,

under these conditions, be dependent on the area of magnesium covered by the reduced metal.

Autoperiodic Systems.

With a view to obtain periodic phenomena from the simplest reacting systems, continuous measurements of the electro-potential of single activated metals reacting with a suitable solution have been made. The object has been to dispense with a separate second metallic component and incorporate it with the dissolving metal, causing the reacting electrode to function as its own activating agent.

Some experiments were carried out with aluminium, magnesium, and zinc after treatment by the usual methods. Aluminium, after vacuum-heat treatment or after scraping, in dissolving in hydrochloric acid registered a fluctuating potential, and a similar behaviour was noticed in the case of magnesium after vacuum-heat treatment. Magnesium gave a perfectly steady reading after scraping and attempts to activate zinc by either method were unsuccessful. The fluctuations were of the order of 0·02 volt and were rather rapid and very irregular, but the potential–time curve was very different from that obtained in the case of ordinary untreated aluminium or magnesium in hydrochloric acid. The changes were too small to affect the gas pressure.

The positive results served to demonstrate the possibility of constructing autoperiodic systems, though these particular cases did not lend themselves to quantitative development. The feeble activation which could be induced in these metals was very probably on account of the difficulty in hardening them and for this reason subsequent attention was devoted to copper, which has been found easily susceptible to activation. In all the experiments cited below, the copper was activated by cold rolling to the specified thickness from an original thickness of 0·022 in.

Activated copper, dissolving in nitric acid, showed no sign of periodicity, but continuous observation over the course of several hours of the potential of activated copper in hydrochloric acid revealed a slow oscillation—about one wave per hour. Copper slowly dissolves in hydrochloric acid containing atmospheric oxygen. By substituting nitric acid for the oxygen, attempts were made to increase the frequency.

Graph 21 was obtained from copper (rolled out to 0·0105 in.) dissolving in an acid mixture containing 25 c.c. of nitric acid (*d* 1·42), 10 c.c. of hydrochloric acid (*d* 1·16), and 65 c.c. of water. The graph illustrates the synchronous periodic variation in the potential of the copper electrode and in the pressure of the evolved

gas. The negative pressures recorded require some explanation: the gas evolved consists mainly of nitric oxide, which reacts with atmospheric oxygen with decrease in volume of the gaseous system as a whole. The fine capillary delays the entry of air and the pressure of gas in the apparatus is therefore slightly below atmospheric.

The series of changes to be observed at the surface of the dissolving metal under these conditions is most striking. Initially, the surface preserves its natural colour: then there is a sudden appearance of a black film deposited in the form of vertical streaks: the black film next turns dull grey: this is followed by a sudden flash due to the film turning white: the film then dissolves, leaving the metal with its original colour. Then the black film forms again, the whole cycle being repeated in each oscillation. After the point where the amplitude of the waves suddenly decreases (see Graph 21), the oscillation is between the black and the grey film, and the white film no longer appears; finally, the black film becomes permanent and the pulsations cease. This cessation is due not to any change in the metal but to a change in the composition of the solution during the progress of the reaction, for when the metal, in this final state, is removed from the solution and placed in a new acid mixture the oscillations recommence. The onset of the black film is marked by a movement of the electropotential in the positive direction and by an increase in the rate of evolution of gas, whilst, corresponding with the gradual turning grey of the film, the electropotential and the gas pressure slowly move towards their former values. The sudden appearance of the white film is accompanied by a rapid change of the electropotential in the negative direction and an equally rapid increase in the rate of gas production. The latter effect is easily visible, resembling a miniature eruption. As the white film dissolves, both the electropotential and the gas pressure regain their initial values.

The limits between which the concentration of the various components of the solution can be varied are narrow. Thus, the mixture 25 c.c. of nitric acid, 10 c.c. of hydrochloric acid, 65 c.c. of water always produced the periodic phenomena when acted on by rolled copper, but, if the total volume of solution was kept constant at 100 c.c. and the amount of hydrochloric acid at 10 c.c., mixtures containing 30 c.c., 20 c.c., or 27·5 c.c. of nitric acid did not favour the production of periodicity. Similarly, if the amount of nitric acid was kept constant at 25 c.c. and the total volume again at 100 c.c., mixtures made up with 15 c.c., 5 c.c., or 12·5 c.c. of hydrochloric acid did not give a periodic reaction. For this reason, in order to secure uniform conditions throughout the experi-

ments, a large stock of the standard acid mixture was made up and 100 c.c. were withdrawn for each experiment. Other more widely divergent mixtures were tried, but in these cases the reaction pursued a quite steady course. The concentration of the two acids being kept in the optimum ratio, 25 c.c. of nitric acid : 10 c.c. of hydrochloric acid, the best effect is produced by using 70 c.c. of water, thus making the total volume 105 c.c. No periodicity was observed when the amount of water used was 45 c.c. or 55 c.c. Using 75 c.c. of water, the electropotential and the gas evolution both became periodic, but the film forming over the copper surface alternated between the grey and white forms, the black film never appearing, and the frequency was higher than in the preceding experiments. Thus, under different conditions, the oscillation may be between the grey and white, grey and black, or black and white films : in the former two cases, the amplitude of the electrical effect is correspondingly smaller.

Some experiments have been performed with copper rolled to different thicknesses from the original 0·022 in. sheet. The unrolled copper was incapable of furnishing a periodic reaction under these conditions. Similarly, a piece which had suffered slight deformation by rolling to 0·020 in. was non-periodic. The other specimens, which were rolled to 0·010 in., 0·009 in., 0·0085 in., 0·007 in., and 0·004 in., respectively, all produced the periodic phenomenon and at approximately the same frequency. A sample of the 0·0085 in. copper, after keeping for 3 days, retained its inherent periodicity unabated.

Summary.

Some typical examples of periodic reactions which have been described previously by the authors have now been investigated from the electrochemical standpoint, using an apparatus in which the electrical and chemical effects of the reactions could be registered simultaneously. In the case of activated metallic couples dissolving in hydrochloric acid or ammonium chloride, the difference of potential between the couple as a whole and the solution, and between the two components of the couple undergo periodic fluctuations which synchronise with the periodic evolution of gas. A difference of potential exists between the activated and inactive forms of a metal. Some new reactions, involving the periodic deposition of metals, are described. The change consists in an alternate formation and dissolution of a metallic film which is accompanied by a corresponding oscillation of the electropotential. In some cases, the rate of evolution of hydrogen is also periodic. Examples are given of "autoperiodic" reactions, where one electrode serves both as the reacting metal and as the activating

agent. The best case is furnished by copper, activated by cold rolling, dissolving in a mixture of nitric and hydrochloric acids: this example furnishes very regular waves representing both the electropotential and the pressure of the evolved gas. This is accompanied by a striking series of visible changes in a film formed over the metal surface. The effect of varying the concentration of acids has been studied and the optimum mixture consists of 25 c.c. of nitric acid (*d* 1·42), 10 c.c. of hydrochloric acid (*d* 1·16), and 70 c.c. of water.

The results of several previous experimenters are correlated with the authors' investigations on periodicity as a general principle.

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THE UNIVERSITY, MANCHESTER. [*Received, February 12th*, 1925.]

CXL.—*The Photochemical Decomposition of Nitrosyl Chloride.*

By EDMUND JOHN BOWEN and JOHN FREDERICK SHARP.

THE photochemical decomposition of nitrosyl chloride has been studied by Kiss (*Rec. trav. chim.*, 1923, **42**, 665). Our experiments on the application of the photochemical equivalence law seem to throw light on the mechanism of the decomposition, and to offer an opportunity for a criticism of the interpretation placed by Kiss on his results.

Nitrosyl chloride was prepared in sealed all-glass apparatus by gently warming dry sodium chloride with nitrosylsulphonic acid and condensing the gas in a freezing mixture. The liquid was fractionated and the vapour allowed to fill a glass bulb connected to an all-glass manometer of the Jackson type (J., 1911, **99**, 1066), which had been thoroughly exhausted with two mercury vapour pumps backed by a Hyvac oil pump, the bulb being then sealed off from the vessel containing the liquid. An arm connected to the bulb contained phosphoric oxide, so that the gas, which had already passed over phosphoric oxide, was further dried *in situ*. The bulb was illuminated by the light from an automatically regulated carbon arc (10 amp.), passing through a condenser, a trough of dilute copper sulphate solution, and a gelatin colour filter. The reaction was followed by the change of pressure, the

glass manometer being sensitive to 0·15 mm. The amount of decomposition was measured at intervals up to 10 minutes, being then about 10%, experiment showing that the rate of the back reaction $2NO + Cl_2 \longrightarrow 2NOCl$ over this range was negligible compared with the photochemical decomposition rate. The light absorption remained constant over this range, and the decomposition curve was linear, except for an initial acceleration lasting about 3 minutes, due to thermal expansion. This thermal expansion could not be eliminated by immersing the bulb in water, but could easily be eliminated graphically.

The energy in the light passing the filters, the absorption by the gas (about 90%), and the reflection losses (10%) from the glass surfaces were measured directly with a Moll thermopile connected to a millivoltmeter. This was calibrated by means of Leslie cubes containing boiling water and boiling aniline, allowance being made for the fact that lamp-black surfaces emit and absorb only 90% of black-body radiation, and the usual precautions being taken.

The following is a table of results, each value being a mean rate of change deduced from the linear part of the curve of a complete experiment. In order to produce a sufficiently rapid change to avoid the influence of the back reaction, filters allowing a large range of wave-lengths to pass were necessary. The number of quanta are calculated for a mean wave-length 4700 Å., *i.e.*, $h\nu = 4{\cdot}2 \times 10^{-12}$ erg. Calibration of thermopile: 1 millivolt $= 4{\cdot}45 \times 10^{-5}$ erg per second. Initial pressure of NOCl = 456 mm.

Spectral range of light. Å.	Pressure change per min. in mm.	Molecules decomposed per second.	Quanta absorbed per second.	Ratio: $\frac{\text{Quanta}}{\text{Molecules.}}$	
5000—4380	3·3	$4{\cdot}11 \times 10^{17}$	$8{\cdot}34 \times 10^{17}$	2·03	Bulb in const. temp. bath.
,,	3·1	3·85 ,,	8·34 ,,	2·17	,, ,,
,,	3·8	4·74 ,,	10·1 ,,	2·13	
,,	4·3	5·28 ,,	10·1 ,,	1·91	
5200—4480	2·5	3·11 ,,	6·5 ,,	2·09	Bulb in const. temp. bath.
,,	3·0	3·74 ,,	7·9 ,,	2·11	

Two quanta appear to be absorbed for each molecule decomposed. This makes it likely that the process is a true unimolecular reaction, $NOCl + h\nu \longrightarrow NO + Cl$, followed by spontaneous reactions re-forming nitrosyl chloride, such as the removal of chlorine atoms giving the transitory compound $NOCl_2$ suspected by Trautz and Hinck (*Z. anorg. Chem.*, 1916, **97**, 127) in measurements of the thermal combination of nitric oxide and chlorine.

The heat of formation of nitrosyl chloride is 18,000 cal. (Trautz

and Hinck), from which, taking the heat of dissociation of chlorine as 54,000 cal., we have :

$$NOCl + 45{,}000 \longrightarrow NO + Cl;$$

that is, the minimum wave-length capable of dissociating nitrosyl chloride is 6270 Å. This point is almost exactly where the absorption of nitrosyl chloride begins; the substance having weak bands from 6200 to 5300 Å., strong absorption beginning at 5250 Å. (Magnanini, *Z. physikal. Chem.*, 1889, **4**, 427). Attempts to show that absorption by the red bands of nitrosyl chloride lead to dissociation were unsuccessful because of the small amount of light absorbed.

The above conclusion is not in accordance with Kiss's interpretation. Using white light, and carrying the decomposition further, he calculates constants from his results from a knowledge of the back reaction and assuming that the decomposition follows a unimolecular equation. On the present view, which is the only one compatible with the quantum mechanism of the process, the decomposition, though unimolecular in essence, will proceed at a rate determined by the amount of light absorbed. The light absorbed cannot have varied appreciably in Kiss's experiments, in which the maximum decomposition was about 10%; and in fact recalculation of his results assuming that the decomposition rate is constant, involving a 10% increase near the end of the reaction, greatly improves his constants.

One other conclusion of Kiss's must be criticised, namely, his very remarkable statement that the rate of combination of nitric oxide with chlorine is uninfluenced by light. If the photochemical change does take place and obeys the equivalence law, then the rate in his experiments should be

$$\text{Rate of decomp. of NOCl} \times \frac{\text{Cl}_2 \text{ absorption in white light}}{\text{NOCl absorption in white light}}.$$

In Kiss's experiments, the first quantity is 0·3 mm. per minute, while the ratio of absorptions will be very small, say 1/20. Kiss's measured rate of thermal combination is 10 mm. per minute, from which it is clear that any photochemical change will be completely undetected when superimposed on the rapid thermal rate.

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant which facilitated this work.

BALLIOL AND TRINITY PHYSICAL CHEMISTRY LABORATORY,
OXFORD. [*Received, March 6th*, 1925.]

CXLI.—*The Mercuration of Aromatic Substances. Part I. Toluene.*

By SAMUEL COFFEY.

LITTLE of the considerable amount of research that has been done on the mercuration of benzenoid compounds is of a quantitative character and some misconceptions of the positions taken up by the entering group appear to exist. Whitmore ("Organic Compounds of Mercury," 1921, p. 194) states that mercury apparently never enters the nucleus in the meta-position to an orienting group, but Holleman (private communication) has found that the mercuration product of nitrobenzene contains 40% and 50% of the *m*- and *o*-isomerides, respectively. The present investigation has been undertaken with the view of obtaining more quantitative information on these matters. Dimroth (*Ber.*, 1899, **32**, 761) has shown that toluene is easily mercurated and claims to have isolated *o*- and *p*-chloromercuritoluenes. Steinkopf (*Annalen*, 1917, **413**, 329), repeating the work, could not obtain pure products. The problem has now been more thoroughly investigated on quantitative lines.

Pure toluene was mercurated and after partial separation of the monomercuri- from the polymercuri-compounds the former were converted quantitatively into a mixture of bromotoluenes, which thermal examination showed to be a ternary mixture containing a considerable quantity of *m*-bromotoluene (compare van der Laan, *Rec. trav. chim.*, 1907, **26**, 29). The bromotoluenes were oxidised with dilute nitric acid to the bromobenzoic acids (compare Cohen and Miller, J., 1904, **85**, 174; Cohen and Dutt, J., 1914, **105**, 504), which were separated from one another by a method based on that described by Holleman (*Rec. trav. chim.*, 1915, **33**, 184).

A preliminary quantitative study of the oxidation by nitric acid of the three monobromotoluenes separately showed that the total bromotoluene could be accounted for and that the yields of the three acids were: *o*-, 87%; *m*-, 90%; *p*-, 92%.

By the method of separation used, which was extremely laborious, from 10 g. of the mixed acids there were obtained, in round figures, 4·5 g. of *p*-bromobenzoic acid and 1·3 g. of *m*-bromobenzoic acid. If, as is most likely, the remainder was the *o*-isomeride, and allowance be made for the different yields of bromobenzoic acids obtained by oxidation of the three bromotoluenes, the proportions of the three constituents of the mixture, and hence also of the three acetoxymercuritoluenes in the product of mercuration of toluene, are: $o : m : p = 43 : 13 : 44$.

This result is interesting, for in the bromination, nitration, and sulphonation of toluene the yield of *m*-compound is less than 5%. Taken in conjunction with Holleman's discovery mentioned above, it indicates that the course of mercuration is not dependent solely on the group already present.

EXPERIMENTAL.

Preparation of Pure Toluene.—The homogeneous mixture obtained by heating together pure *p*-toluenesulphonamide (100 g.), sulphuric acid (85 g.), and water (40 g.) at 200—210° was distilled with superheated steam at 200—220° until toluene ceased to pass over (3 hours). The oil was washed with sodium hydroxide solution, dried, and distilled (yield 45 g.; 83%). The toluene obtained on redistillation boiled within 0·1° at 109·4°/743 mm. and had a sweet aromatic odour quite unlike the sooty smell usually associated with this compound.

Mercuration of Toluene and Partial Separation of the Products.—Toluene was heated under reflux with mercuric acetate ($\frac{1}{5}$ part) for 5 or 6 hours. After 12 hours, the liquid was decanted, the insoluble polymercurated toluene washed with toluene and a little acetic acid, and the solution and washings were distilled until the temperature was 120°. The residue was poured into a solution of potassium bromide, the remaining toluene distilled as rapidly as possible in steam, and the bromomercuritoluenes were collected, washed, and dried. Attempts to determine the mercury in this mixture by the usual rapid methods were unsuccessful. The amount of polymercurated toluene obtained (as chlorides) from the insoluble product of the reaction was less than one-tenth of the yield of crude bromomercuri-compounds. All the mercuric acetate was accounted for as mercurated toluene.

Conversion of the Bromomercuritoluenes into Bromotoluenes.—The bromomercuritoluenes, suspended in well-cooled chloroform, reacted almost instantly with bromine (1 equiv.), added slowly. After filtration, the mercuric bromide was washed with chloroform, the solvent removed from the filtrate and washings on the water-bath, and the bromotoluenes were distilled in steam and fractionally distilled three times, the fractions finally obtained from 74 g. of the crude bromomercuri-compounds being: 181—190°, 25 g. (temperature rose very rapidly from 186° to 190°); 190—210°, 2 g.; 210—250°, 2·5 g.; and above 250°, 1 g.

The main fraction consisted of pure monobromotoluenes and the remainder of dibromotoluenes (b.p. 230—245°), but there was no substitution in the side chain. The crude monobromomercuritoluenes prepared in this way are therefore considerably con-

taminated with polymercurated compounds (roughly 15%). About 95% of the bromomercuri-compounds were accounted for. The main fraction of monobromotoluenes showed a well-defined freezing point at −10·8°, a second less marked one at −53°, and was still partly liquid at −78°. Hence it was a mixture of all three isomerides, not a simple mixture of ortho- and para-isomerides, which gives a eutectic at −38°.

Oxidation of the Monobromotoluenes.—The pure bromotoluenes were prepared from specially purified amines by van der Laan's method (*loc. cit.*). The *p*-bromotoluene melted at 26·4° instead of 26·7° and the *o*-compound at −27° instead of −26°.

The bromotoluene (2 g.) was heated with 10 g. of dilute nitric acid ($1HNO_3 : 3H_2O$) at 130° for 8 hours (Cohen and Miller, *loc. cit.*). The product was neutralised with caustic potash, the small amount of insoluble oil (mainly, if not wholly, bromonitrotoluenes) removed with ether, and the acids were precipitated with nitric acid and dried in a vacuum; a further small quantity was extracted from the aqueous solution with ether. The small amount of hydrogen bromide in the aqueous solution, determined by titration with silver nitrate, was a measure of the bromotoluene which had been completely oxidised.

The results given in the table are the means obtained from several concordant determinations.

Bromotoluene.	% insol. in ether.	% as free HBr.	% as acid.
Ortho	5·4	10·0	87·2
Meta	4·4	2·3	90·0
Para	1·4	3·9	92·4
Mixed	3·4	6·6	91·2

Separation of the Bromobenzoic Acids.—Preliminary experiments showed that boiling saturated aqueous solutions contain about 4%, 1·0%, and 0·15% of the *o*-, *m*-, and *p*-acid respectively, and that the solubilities of the barium salts are: at 18°, *o*-, 23%; *m*-, 0·65%; *p*-, 0·85%: at 100°, *m*-, 3·4 g., and *p*-, 2·25 g., per 100 c.c.; yet the *p*-salt is described in the literature as readily soluble.

The mixture of acids obtained above (10 g.) was extracted thrice with 200 c.c. of boiling water for 3 hours. The residue (3·70 g.), m. p. 256°, was pure *p*-bromobenzoic acid (the m. p. of which is usually given as 251°).

The aqueous extracts were neutralised with baryta, gradually evaporated and allowed periodically to crystallise. Mixtures of barium salts separated in characteristic nodules until the volume of the solution was 30—40 c.c., when the readily soluble ortho-salt began to crystallise. The mixture of barium salts was crystallised

from water six or more times, when the pure *m*-salt was obtained. (A mixture of barium *m*-bromobenzoate with a small quantity of the *p*-isomeride behaved similarly.) The sparingly soluble barium salts were dissolved in water and fractionally precipitated with *N*/10-hydrochloric acid, first, impure *p*-acid and then impure *m*-acid being obtained. Finally, 0·6 g. of pure *p*-bromobenzoic acid was isolated, making 4·3 g. altogether. The impure *m*-acid was again converted into the barium salt, the latter systematically crystallised to free it from the readily soluble *o*-salt, and then reconverted into the acid, which was recrystallised once from water. Altogether 1·20 g. of acid melting at 145—149° were obtained; a mixture of *m*-bromobenzoic acid and 10% of the *p*-isomeride also melted at this temperature, and a mixed melting point gave 145—149°. By continued fractionation of the barium salts pure *m*-bromobenzoic acid was obtained. Thus 4·42 g. of *p*-bromobenzoic acid and 1·08 g. of the *m*-isomeride were isolated from 10 g. of the mixed acids. The mother-liquors (45 c.c.) containing the *o*-salt probably contained barium salt equivalent to 0·2 g. of the *m*-acid. The total quantity of *m*-bromobenzoic acid present in 10 g. of the mixed acids was therefore about 1·3 g.

The mother-liquors containing the very soluble barium salts gave on acidification a good yield of impure *o*-bromobenzoic acid.

In conclusion, the author wishes to express his thanks to the Ramsay Memorial Trustees for the grant of a Fellowship which has enabled him to carry out this work.

THE RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, December 20th*, 1924.]

CXLII.—*A Synthesis of* 1:2-*Dihydroquinaldine.*

By FREDERICK ALFRED MASON.

1:2-DIHYDROQUINALDINE, which was prepared by Räth by heating together *o*-toluidine and α-chloropropaldehyde diethylacetal (*Ber.*, 1924, **57**, 555), has now been synthesised by a method * employing cheap and readily obtainable materials. Aniline condenses with β-chlorobutaldehyde diethylacetal, under the conditions stated later, to give β-*anilinobutaldehyde diethylacetal*, which is

* The investigation was begun in 1923 before the publication of Räth's results, but had to be suspended for some time and was completed in 1924.

converted into 1:2-dihydroquinaldine by treatment with phosphoric anhydride in benzene solution:

$$CHMeCl\cdot CH_2\cdot CH(OEt)_2 \xrightarrow{NH_2Ph} NHPh\cdot CHMe\cdot CH_2\cdot CH(OEt)_2 \xrightarrow{-2EtOH} C_6H_4\langle \begin{matrix} CH{=}CH \\ NH\cdot CHMe \end{matrix}$$

Attempts to close the ring by means of strong or dilute hydrochloric acid, glacial acetic acid or acetic anhydride gave negative results.

β-p-*Ethoxyanilinobutaldehyde diethylacetal*,

$$CHMe(NH\cdot C_6H_4\cdot OEt)\cdot CH_2\cdot CH(OEt)_2,$$

obtained by using *p*-phenetidine in place of aniline, on treatment with phosphoric anhydride in benzene solution, gave a small amount of an oil, b. p. 260—270°, which did not appear to be the expected *p*-ethoxydihydroquinaldine.

Aniline and crotonaldehyde diethylacetal were heated together in alcoholic solution, but β-anilinobutaldehyde diethylacetal could not be detected in the product. Attempts to condense aniline with β-chlorobutaldehyde diethylacetal by means of sodium amyloxide also failed, the product consisting, probably, of a mixture of aniline and crotonaldehyde diethylacetal, so that here also there was no evidence that aniline could add on to the nascent double bond. This is of interest as indicating that in the Doebner-Miller quinaldine synthesis the reaction probably takes place according to equation (1) rather than (2) (compare Blaise and Maire, *Bull. Soc. chim.*, 1907, **3**, 667):

$$CHMe{:}NPh + H\cdot CH_2\cdot CH{:}NPh = CHMe(NHPh)\cdot CH_2\cdot CH{:}NPh \quad (1)$$
$$CHMe{:}CH\cdot CHO + 2NH_2Ph = CHMe(NHPh)\cdot CH_2\cdot CH{:}NPh + H_2O \quad (2)$$

Neither quinaldine nor dihydroquinaldine was recognised in the product obtained on heating together aniline and β-chlorobutaldehyde diethylacetal in the way used by Räth for his synthesis.

EXPERIMENTAL.

β-Chlorobutaldehyde diethylacetal was prepared from crotonaldehyde and absolute alcohol saturated in the cold with hydrogen chloride, by Wohl and Frank's method (*Ber.*, 1902, **35**, 1904). The yield was only about 50% (Wohl claimed 66%), but no improvement was effected by the addition of calcium chloride or otherwise varying the conditions.

β-*Anilinobutaldehyde Diethylacetal*.—A mixture of freshly-distilled β-chlorobutaldehyde diethylacetal (25 c.c.), dry amyl alcohol (50 c.c.), powdered, well-dried potassium carbonate (25 g.), copper

powder (1 g.), and sodium iodide (2 g.) was shaken and kept for 5 minutes and, after addition of redistilled aniline (13 c.c.), heated under reflux for 48 hours. The cooled liquid was filtered, the residue washed with a little amyl alcohol, and the combined filtrates were distilled until the amyl alcohol was removed; the distillation was then continued at 25 mm. and gave the following fractions: 100—150°, 25 c.c.; 150—170°, 18 c.c.; 170—190°, 3 c.c. After refractionation, 18 c.c. of a clear yellow, slightly viscous oil were obtained, b. p. 173—175°/25 mm. or 153—154°/12 mm. Yield 17·9 g. or 56% (Found: C, 70·8; H, 9·7; N, 5·9. $C_{14}H_{23}O_2N$ requires C, 70·9; H, 9·7; N, 5·9%).

The substance gave, in ethereal solution, a yellow *picrate* crystallising from alcohol in yellow spangles, m. p. 188—190°, and in dilute hydrochloric acid a yellow precipitate with platinic chloride which quickly became tarry.

In one experiment, the copper powder was omitted, but the yield remained about the same; in other cases again, although the experimental conditions were apparently the same, the yield was practically negligible, the product consisting of viscous, high-boiling gums.

β-p-*Ethoxyanilinobutaldehyde diethylacetal* was prepared in a similar manner to the anilino-compound, using β-chlorobutaldehyde diethylacetal (55 c.c.), amyl alcohol (75 c.c.), potassium carbonate (50 g.), sodium iodide (4 g.), and *p*-phenetidine (41 g.), but no copper powder. The mixture having been heated under reflux for 28 hours, and the product fractionated, 56 g. of the acetal were obtained, b. p. 190—192°/12 mm. (yield 68%). It formed a pale yellow, slightly viscous oil which was slightly heavier than water (Found: C, 68·3; H, 9·7. $C_{16}H_{27}O_3N$ requires C, 68·3; H, 9·6%). With an ethereal solution of picric acid, it gave an orange-yellow coloration, but no picrate separated.

An attempt to prepare the *p*-chloroanilino-compound gave no definite product except a very small amount of a substance which, after recrystallisation from alcohol, melted at 95—97°.

1 : 2-*Dihydroquinaldine.*—β-Anilinobutaldehyde diethylacetal (10 c.c.) was dissolved in well-dried benzene (50 c.c.) and phosphoric oxide (10 g.) was added by degrees. After standing over-night at room temperature, the mixture was heated under reflux for 6 hours and cooled, and ice and water were added until practically all was in solution. The aqueous layer was washed with benzene, made alkaline with ammonia, the oil extracted twice with ether and dried over potassium carbonate. The product on fractionation at 20—25 mm. gave 3 c.c., b. p. 130—160°, which after refractionation gave 2·2 c.c. of a pale yellow liquid, b. p. 125—130°/18 mm.

(Found: C, 82·7; H, 7·6; N, 9·7. Calc., C, 82·8; H, 7·6; N, 9·6%). It had an odour resembling that of quinaldine, decolorised permanganate, and agreed generally with Räth's description of the substance.

The oil darkened on keeping in a sealed tube and formed a picrate melting at 192—193°, after recrystallisation from alcohol.

An attempt was made to close the ring of *p*-ethoxyanilinobutaldehyde diethylacetal (10 c.c.) in a similar manner. About 2 c.c. of an oil were obtained, b. p. 260—270°/760 mm. It formed a picrate, m. p. 190°.

Treatment of the oil with a few drops of cold concentrated hydrochloric acid gave a crystalline hydrochloride, m. p. 234—236° (decomp.), after recrystallisation from a very little methyl alcohol, in which it was extremely soluble. The chlorine found (20·6%) did not correspond to any simple expected derivative (*p*-ethoxydihydroquinaldine hydrochloride contains only 15·7% Cl). The quantity obtained did not suffice for a complete analysis.

Attempt to Condense Aniline and Crotonaldehyde Diethylacetal.—On heating together under reflux the acetal (prepared in 80—90% yield by Frank and Wohl's method) and aniline for 6 hours and distilling the product, neither dihydroquinaldine nor anilinobutaldehyde diethylacetal was found, nor on heating the distillate with sodamide was either of these products detected.

On heating together aniline (28 c.c.) and β-chlorobutaldehyde diethylacetal (25 c.c.) in a sealed tube at 220° for 5 hours (compare Räth's method), a dark brown oil was formed which, on being worked up, gave the following fractions at 20 mm.: 90—110°, 8·5 c.c.; 110—150°, 9 c.c.; 150—165°, 3 c.c.; together with a large amount of tar. The middle fraction afforded a picrate which melted at 170° and was therefore not dihydroquinaldine.

A mixture of aniline and β-chlorobutaldehyde diethylacetal, left in a sealed tube at room temperature for 5 months, became pasty with fine needles of aniline hydrochloride; as all the residue, however, distilled below 100°/40 mm., very little condensation can have been effected and the aniline probably merely removed hydrogen chloride to give crotonaldehyde diethylacetal.

The author's thanks are due to Prof. W. H. Perkin, F.R.S., and the British Dyestuffs Corporation Ltd. for permission to publish the results.

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CXLIII.—*The Hydrates of Calcium Carbonate.*

By JOHN HUME.

IN "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," where there is given (1923 ed., vol. iii, p. 824) a list of references to investigations of the hydrated forms of calcium carbonate carried out since 1819, Mellor sums up the evidence for the existence of various hydrates in the following sentence: "With indecisive evidence of this nature, it appears as if there is a di- or tri-hydrocalcite, and a penta- or hexa-hydrocalcite, or, possibly, mixtures of colloidal calcium carbonate with the anhydrous salt." Copisarow (J., 1923, **123**, 785) describes the preparation of crystals of calcium carbonate pentahydrate and states that no crystalline modification having the composition $CaCO_3,6H_2O$ recorded by Pelouze (*Compt. rend.*, 1865, **60**, 429) could be detected. Mackenzie (*ibid.*, 2409) has shown that $CaCO_3,6H_2O$ can be prepared in 10% sugar solution between 0° and 10°, but he was unable to determine the temperature of transition from the hydrated to the anhydrous state.

In the present work, begun with the object of ascertaining what hydrates actually exist and the conditions necessary for their existence, the crystals were prepared in, and kept in contact with, a 20% aqueous solution of sucrose. In this solution, a hexahydrate exists below 10·4°, and a pentahydrate below 17·0°. The hexahydrate in contact with water at or above 0° changes slowly into anhydrous calcium carbonate (compare Johnstone, Merwin, and Williamson, *Amer. J. Sci.*, 1916, **41**, 471). The same is probably true of the pentahydrate. All dilatometer experiments have shown a break at 25° in the volume–temperature curve, and this suggests that a hydrate lower than the pentahydrate may exist, but, so far, all attempts to obtain confirmation have failed. Under the experimental conditions, the temperatures of transition were quite definite, but possibly they would be altered by varying the concentration of the sugar solution. It is also possible that the hydrates may be metastable even in contact with sugar solution, and may decompose exceedingly slowly.

The formation of crystals of the hexahydrate from sugar-lime solutions at temperatures up to 17° (Mackenzie, *loc. cit.*) has been confirmed. It is explained by the fact that between 10·4° and 25·0° the metastable hexahydrate is first precipitated, and changes slowly into the form stable at the temperature of the experiment.

EXPERIMENTAL.

The hexahydrate crystals were, as a rule, prepared as follows: A solution of sucrose (25 g.) in water (100 c.c.) was shaken with

calcium oxide (freshly prepared from precipitated calcium carbonate) and filtered as quickly as possible to prevent absorption of much carbon dioxide. Carbon dioxide was bubbled through the filtrate at 0° for 5—10 minutes, no precipitate forming, and the solution was then exposed at 0° to the action of atmospheric carbon dioxide. After 2 or 3 days, well-defined crystals separated, which could be preserved in sugar solution for a considerable period (possibly indefinitely) if the temperature were kept down; crystals kept thus for 7 weeks showed no loss of water on analysis. In other experiments, the sugar concentrations were 50 g., 30 g., and 20 g. in 100 c.c. of water, and in each case crystals of the hexahydrate were obtained at 0°. Mackenzie (*loc. cit.*) obtained the same product from more dilute solutions.

The largest crystals were best obtained by omitting the passage of carbon dioxide and allowing the lime-sugar solution to absorb carbon dioxide very slowly from an atmosphere poorer in carbon dioxide than the laboratory air.

Many preparations were made and the crystals were washed with iced water, with absolute alcohol, and with ether, thrice in each case (Found: loss at 100°, 50·3, 49·9, 50·4, 51·6, 50·8, 49·6, 52·7, 49·4, 51·4, 50·3. Calc. for $CaCO_3,6H_2O$: H_2O, 51·9; for $CaCO_3,5H_2O$: H_2O, 47·4%).

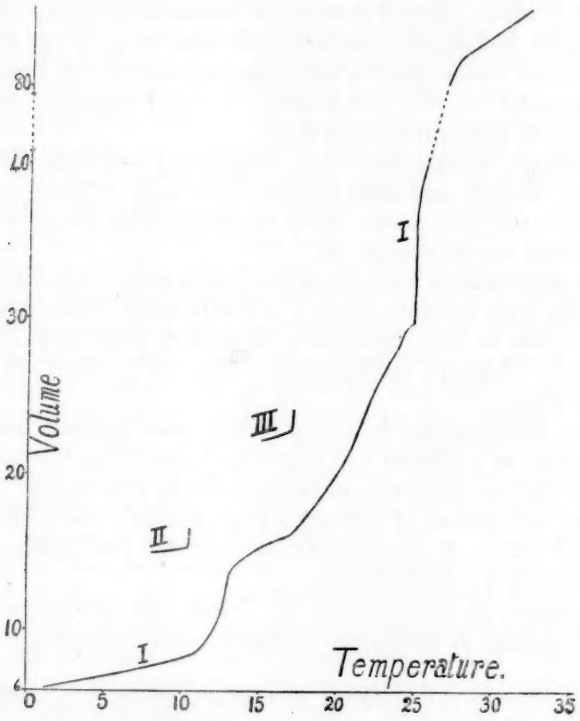
In two analyses, the following results were obtained by heating the crystals in a stream of oxygen and absorbing the water in a calcium chloride tube, the carbon dioxide in a soda-lime tube, and weighing the residue of calcium oxide (Found: CaO, 27·45, 27·3; CO_2, 21·5, 22·3; H_2O, 51·5, 50·3. Calc. for $CaCO_3,6H_2O$: CaO, 26·9; CO_2, 21·1; H_2O, 51·9%).

The density of the crystals, $d^{15°}$ 1·789, was determined by the floating method in methylene iodide–benzene (compare Mackenzie, *loc. cit.*).

To investigate the stability of the hexahydrate in contact with water, crystals of known water-content were kept in water at 0° and samples were withdrawn from time to time and analysed [Percentage of water found: (i) initial, 49·6; after 7 days, 5·6. (ii) initial, 52·7; after 8 days, 5·3. (iii) initial, 49·4; after 2 days, 39·8; after 4 days, 14·7].

The results showed that it was useless to carry out dilatometric experiments with the crystals in contact with water. Accordingly, to determine whether the hexahydrate changed into lower hydrates at temperatures above 0°, the crystals and their mother-liquor were placed in a dilatometer, specially designed for easy filling at temperatures below atmospheric (Hume, *Chem. News*, 6th June, 1924). The temperature had to be raised exceedingly slowly, and

it was necessary to design a modified thermo-regulator for the purpose (Hume, *J. Soc. Chem. Ind.*, 1924, **43**, 250). Many temperature and volume readings were taken, and the curves plotted from the data of three experiments are reproduced. A blank experiment was done with sugar solution of the same concentration as was used in the preparation of the crystals, and this gave a normal expansion curve.



Curve I (crystals prepared at 0°) shows a transition beginning at about 11·3°, and another at about 17·3°. The latter involved a large volume change, and before it was quite complete the temperature reached 25°. Here an even larger increase of volume was observed. After expansion ceased, the crystals contained 0·7% of water.

Curve II (crystals prepared at 0°) shows the results of an experiment in which the temperature was raised at the rate of 0·1° per day. The first break in the curve is at 10·4°. When constant volume was reached at this temperature, the crystals contained 47·5% of water. A density determination by floating the crystals

in methylene iodide and benzene at 15° gave the value 1·835. The crystals from a duplicate experiment had a water-content of 47·0% and a density of 1·833.

Crystals prepared by the method described above for the hexahydrate, but at 11·6°, contained 47·2% of water and had $d^{15°}$ 1·830 and 1·833. A sample of these crystals was used for a dilatometer experiment; the results, given in Curve III, show a transition beginning at about 17°.

All attempts to prepare a definite hydrate from sugar-lime solutions kept at 18° were unsuccessful. Fresh hexahydrate crystals were therefore introduced into two dilatometers, kept at 24°. Expansion took place for 4½ months, and when it ceased, the crystals were anhydrous, and of density 2·6. No confirmation, therefore, of the existence of a trihydrate, or of any hydrate lower than a pentahydrate, was obtained, although such may exist between 17° and 24°. Also the break in the curves at 25° has, so far, not been accounted for.

The crystals obtained when calcium carbonate was precipitated at 0° in glycerol solution and in 10% sodium hydroxide solution contained 51·5% and 51·5% of water respectively.

Attempts were made to determine the vapour pressure of the hexahydrate by keeping crystals of it in an evacuated bulb attached to a manometer. The pressure in the bulb increased to that of saturated water vapour, and thereafter remained constant, while the dehydration of the crystals proceeded to completion. It is therefore concluded that the vapour pressure, or rather the decomposition pressure, of the hexahydrate is above the vapour pressure of water at temperatures above 0°.

Further attempts are being made to isolate a hydrate lower than the pentahydrate, and experiments are in progress to determine the decomposition pressures of the hydrates.

THE UNIVERSITY, LEEDS. [*Received, March 11th*, 1925.]

CXLIV.—*The Interaction of Thiocyanogen with Unsaturated Compounds.*

By FREDERICK CHALLENGER and THOMAS HAROLD BOTT.

THE product obtained from thiocyanogen and styryl methyl ketone (J., 1923, **123**, 1055) is a monothiocyano-substitution derivative, CHPh:C(SCN)·COMe(I). The molecular weight in benzene corresponds with this formula and not with $[COMe·CH(SCN)·CHPh]_2$ (II), whilst the structure SCN·CHPh·CH(SCN)·COMe (III) is

excluded by analysis. Other evidence in this direction is furnished by reduction, oxidation, and the action of bromine (see experimental section). The thiocyano-group is not in the nucleus, whilst the structure $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}SCN$ is improbable. Moreover, distyryl ketone and thiocyanogen give a compound analogous to (I) containing two thiocyano-groups. Here a methyl radical is absent.

From the results described previously (*loc. cit.*), and the work of Kaufmann and Liepe (see J., 1924, **125**, 1377) on the interaction of thiocyanogen with ethylene, amylene, and antipyrine, it is probable that styryl methyl ketone first gives (III), which then loses thiocyanic acid. By analogy with similar reactions, a compound of structure (I) should result. This is in agreement with the work of Dufraisse (*Compt. rend.*, 1920, **171**, 1062; 1921, **173**, 985) and of Pauly and Berg (*Ber.*, 1901, **34**, 2093) on ethylideneacetone dibromide.

The bromostyryl methyl ketone of Ruhemann and Watson (J., 1904, **85**, 456) was assumed by these authors to have the β-structure $CPhBr{:}CH{\cdot}COMe$ by analogy with the bromostyryl phenyl ketone which Wislicenus (*Annalen*, 1899, **308**, 219) regarded as $CPhBr{:}CH{\cdot}COPh$. This has now been shown by Dufraisse (*loc. cit.*) to have the α-structure $CPhH{:}CBr{\cdot}COPh$. Hence it is probable that the product of Ruhemann and Watson also is an α-derivative.

The compound obtained from carvone and thiocyanogen contains only one thiocyano-group. Owing to the very poor yield obtained and the inability of one of us to continue the investigation, the substance has not been further examined. On the assumption that the double bond in the side chain is unattacked the most probable constitution would appear to be

$$CH_2{:}CMe{\cdot}CH{<}\begin{matrix}CH{=}CH\\CH_2{\cdot}CO\end{matrix}{>}C(SCN){\cdot}CH_3,$$

but others are clearly possible.

When styryl methyl ketone dibromide is boiled with alcoholic potassium thiocyanate, the ketone is regenerated, and polymerised thiocyanogen obtained. Wheeler and Merriam (*J. Amer. Chem. Soc.*, 1902, **24**, 441) obtained a similar result with dinitrostilbene dibromide.

Experimental.

α-Thiocyanostyryl Methyl Ketone (I).—Solutions in dry ether of styryl methyl ketone (10 g. [1/15 mol.] in 50 c.c.) and thiocyanogen (Soderbäck, *Annalen*, 1919, **419**, 217) (1/15 mol. in 270 c.c.) were mixed and kept in the dark. After 4 days the ethereal suspension of polymerised thiocyanogen was decanted from the crystalline

product. On fractionation from acetone–ligroin in presence of animal charcoal, 2·5 g. of white, glistening plates were obtained, m. p. 119° (Found: C, 65·2; H, 4·4; N, 7·0; S, 15·85; *M*, cryoscopic in benzene, 185. $C_{11}H_9ONS$ requires C, 65·0; H, 4·4; N, 6·9; S, 15·7%; *M*, 203).

Some unchanged ketone was obtained from the ethereal filtrate, but no other pure product could be isolated.

Thiocyanostyryl methyl ketone is also obtained, but in no better yield, by adding, during 2 hours, 10 g. of iodine in 50 c.c. of ether to 5 g. of styryl methyl ketone, 12·5 g. of mercuric thiocyanate, and 50 c.c. of ether.

Action of bromine. The thiocyano-ketone (2·04 g.) in 30 c.c of carbon disulphide was treated with 1·6 g. of bromine (1 mol.) in 10 c.c. of the same solvent. Decoloration was complete in some hours, but no hydrogen bromide was formed. After four crystallisations from alcohol, the *dibromide* formed long, white needles, m. p. 138° (decomp.) (Found: N, 4·0; Br, 43·25. $C_{11}H_9ONBr_2S$ requires N, 3·85; Br, 44·05%).

Oxidation. (*a*) Aqueous 4% potassium permanganate (100 c.c.) was boiled with 0·4 g. of the ketone for 4 hours, and excess of the reagent removed with hydrogen peroxide. Potassium sulphate, benzoic acid (m. p. 121°), and traces of a fatty acid were produced, but no diphenylsuccinic acid.

(*b*) The ketone (0·5 g.) was shaken for 6 hours with a solution of 1 c.c. of bromine and 4 g. of potassium hydroxide in 80 c.c. of water, and the mixture was extracted with ether and treated with sulphur dioxide. Cinnamic acid (m. p. and mixed m. p. 133°) was deposited.

Reduction. The ketone (1·5 g.) was boiled for 4 hours with 5 g. of zinc dust and 50 c.c. of water, and the mixture, which contained thiocyanate ions, was distilled in steam, giving benzylacetone (m. p. and mixed m. p. of semicarbazone, 131°). The residue, on extraction with alcohol, yielded traces of a solid, m. p. 157°. δε-Diphenyl-βη-octadione melts at 161°.

Distyryl Ketone and Excess of Thiocyanogen.—After 4 days, an ethereal solution of the reactants deposited a solid which, on crystallisation from acetone–ligroin, melted at 151° and gave a deep blue coloration with sulphuric acid (Found: N, 8·2; S, 18·4. $C_{19}H_{12}ON_2S_2$ requires N, 8·05; S, 18·4%).

Carvone and Thiocyanogen.—Carvone (10 g.) was added to a solution of thiocyanogen (see p. 1040). After 4 weeks the solvent was removed, and the oil washed with ligroin and extracted with acetone–ligroin. The concentrated extract was diluted with alcohol, and the white needles (1 g.) deposited after 4 days were crystallised

from alcohol; m. p. 254° (Found: N, 7·0; S, 15·7. $C_{11}H_{13}ONS$ requires N, 6·8; S, 15·5%).

The authors are indebted to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, November 17th*, 1924.]

CXLV.—*The Potassium Chlororutheniates and the Co-ordination Number of Ruthenium.*

By S. H. CLIFFORD BRIGGS.

BY the action of alkali chlorides upon solutions of ruthenium trichloride, Howe (*J. Amer. Chem. Soc.*, 1901, **23**, 775) obtained compounds of the formula $M^{I}_{2}RuCl_5,H_2O$ analogous to the salt K_2RuCl_5,H_2O described by Miolati and Tagiuri (*Gazzetta*, 1900, **30**, 511), and named Miolati's series in the present paper. They give yellowish-brown solutions which are pure yellow when dilute and are not affected by chlorine or bromine vapour. Howe prepared a second series of compounds which are generally regarded as aquopentachlororutheniates with the molecule of water in the complex as shown by the formula $M^{I}_{2}(RuCl_5H_2O)$. These compounds are more soluble than the salts of Miolati's series and give solutions which are pink when very dilute and give an intense black coloration with chlorine or bromine. These compounds will be referred to below as Howe's series.

Since the water in Miolati's salt K_2RuCl_5,H_2O is very firmly attached and not completely given off at 200° (compare Gutbier, Falco, and Vogt, *Z. anorg. Chem.*, 1921, **115**, 230), the water molecule would appear to be a constituent of the complex in both series. As, however, the simple compound $K_2(RuCl_5H_2O)$ cannot exist in two isomeric forms according to the co-ordination theory (compare Briggs, J., 1921, **119**, 1876), it was decided to make a further investigation of the potassium chlororutheniates.

It has been found that in Miolati's series there are at least two compounds having the formulæ K_2RuCl_5,H_2O and $2K_2RuCl_5,3H_2O$ respectively. In Howe's series, the only salt prepared in the pure state had the formula $2K_2RuCl_5,3H_2O$, although some slight evidence was obtained for the existence of other compounds having the formulæ K_2RuCl_5,H_2O and $K_2RuCl_5,2H_2O$.

The compound K_2RuCl_6 obtained by Howe (*J. Amer. Chem. Soc.*, 1904, **26**, 546) from the black solution produced by oxidising Howe's salt $K_2(RuCl_5H_2O)$ with chlorine, was not prepared during the

work now described, but a substance was obtained of which the analysis corresponded closely with the formula $K_2(RuCl_5OH,H_2O)$. As the details given in Howe's papers are very incomplete, it does not follow that the compound K_2RuCl_6 cannot be prepared.

A salt of the formula K_2RuCl_5,K_2RuCl_5OH was produced by the action of a current of air on a warm, acidified solution of the compound $2K_2RuCl_5,3H_2O$ (Howe's series). It would therefore appear that in oxidation by chlorine or oxygen a hydrogen atom is removed from a co-ordinated water molecule, giving a hydroxo-compound.

The Co-ordination Number of Ruthenium in the Chlororutheniates.

It is evident that the co-ordination number of ruthenium is greater than 6 in the compounds $2K_2RuCl_5,3H_2O$, and hexachlororutheniates with constitutional water have recently been prepared by Krauss (*Z. anorg. Chem.*, 1921, **117**, 111) and by Aoyama (*ibid.*, 1924, **138**, 249) having the formulæ Cs_2RuCl_6,H_2O and $2(NH_4)_2RuCl_6,H_2O$, respectively, in which the co-ordination number of ruthenium is also greater than 6.

If water molecules or chlorine ions are shared by the ruthenium atoms it is possible to write the compound $2K_2RuCl_5,3H_2O$ in isomeric forms with co-ordination number 7 (one chlorine atom or water molecule shared) or with co-ordination number 8 (three bridging units shared). It does not appear probable that simple chemical methods will be found for determining the exact nature of these compounds, but an *X*-ray examination of the crystals might help to elucidate the problem, and such an examination is very much to be desired. Since there are exceedingly few co-ordination compounds with co-ordination number 7, in the author's opinion it is likely that the ruthenium atoms function with co-ordination number 8 in the compounds under review, and it should be noted that all the compounds described below might be formulated with this co-ordination number.*

* Attention has been directed to the fact that the co-ordination number 7 is in accordance with the electronic structure of ruthenium. If, however, tervalent ruthenium had the co-ordination number 7 as a result of the completion of the electron sub-groups as required by Sidgwick's theory (J., 1923, **123**, 725), then surely tervalent iron should also give compounds with co-ordination number 7. Now a very large number of complex compounds of tervalent iron have been prepared, but so far as I am aware in all these cases the co-ordination number is 6. If, in the extensive literature, there are to be found any examples with co-ordination number 7, they are certainly an extremely small proportion of the total.

My own view is that there are at least two factors involved in the determination of co-ordination number. One of these is the tendency to form spatially symmetrical compounds due to the fact that the affinity of the

EXPERIMENTAL.

The ruthenium trichloride was purchased from Messrs. Johnson, Matthey and Co. and was free from other platinum metals with the exception of a trace of rhodium. It was used without further purification in the earlier part of the investigation. The material was then worked up and purified by conversion into the tetroxide as described by Howe. The trichloride prepared from the tetroxide gave substances identical with the preparations from the unpurified trichloride.

For analysis, the compounds, after being dried in a vacuum over sulphuric acid, were reduced in a current of pure hydrogen, the evolved gases being led through a delivery tube which just dipped into a solution of silver nitrate slightly acidified with nitric acid and contained in a small wide-mouthed flask. The gases then passed through absorption bulbs containing a further quantity of the silver nitrate solution, which remained clear when the reduction was carefully performed. For accurate results, it was found necessary, after lixiviating the ruthenium residue, to repeat the reduction and lixiviation once or twice.

In some cases, water was estimated directly by combustion over lead chromate as in the analysis of organic compounds containing halogens. It was essential to do the combustion in oxygen. When air was used the results were too low.

Miolati's Series.—The salts of Miolati's series are formed when potassium chloride is added to a cold acidified solution of ruthenium trichloride. The precipitated compound is usually not homogeneous, but by recrystallisation from warm acidified water the compound K_2RuCl_5,H_2O was obtained by Gutbier, Falco, and Vogt

central atom emanates from the nucleus and is directed equally towards all points on the surface of the atomic sphere. Co-ordination numbers 4, 6, and 8 are therefore common, corresponding to the corners of regular polyhedra circumscribed about the surface of the atomic sphere, in accordance with Werner's theory. We may describe this first factor as the *Werner* factor. The second factor, which may be termed the *Sidgwick* factor, is the tendency to form complete sub-groups of electrons as shown by Sidgwick (*loc. cit.*). When the two factors both tend to give the same co-ordination number, very stable and well-defined co-ordination compounds are produced; and it is to such compounds that Sidgwick directs special attention in his paper. In those cases in which the two factors tend to give different co-ordination numbers the Werner factor appears to exert the preponderating influence, and consequently there are very few compounds with co-ordination number 5 or 7. I therefore think it is much more probable that in the compounds described in this paper it will ultimately be found that ruthenium has the co-ordination number 8 rather than 7. Of course there is also the possibility that the series of Howe and Miolati represent compounds with different co-ordination numbers, 7 in one of the series and 8 in the other.—S. H. C. B.

(*loc. cit.*), to whose paper reference should be made for a description of this salt.

During the present investigation, in one case the analysis of the precipitated salt agreed closely with the formula K_2RuCl_5,H_2O. In this preparation, 8 g. of potassium chloride in 30 c.c. of water were added to a cold solution of 5·63 g. of ruthenium trichloride in 130 c.c., sufficient hydrochloric acid being present to cause the solution to fume when heated on the water-bath [Found : Ru, 27·1; K, 20·8; Cl, 46·5; H_2O (diff.), 5·5. Calc., Ru, 27·1; K, 20·9; Cl, 47·3; H_2O, 4·7%].

In another preparation 2·7 g. of potassium chloride in 8·5 c.c. of water were added to a cold solution of 2 g. of ruthenium trichloride in 40 c.c. of hydrochloric acid (*d* 1·1) which had been kept for 2 days, and a precipitate was obtained of the formula $2K_2RuCl_5,3H_2O$ [Found : Ru, 27·05; Cl, 46·1; K, 20·0; H_2O, 6·8 (diff.). Calc., Ru, 26·5; Cl, 46·1; K, 20·35; H_2O, 7·0%]. Another method for the preparation of this salt, $2K_2RuCl_5,3H_2O$ (Miolati's series), is given below (p. 1047).

Howe's Series.—The salt $2K_2RuCl_5,3H_2O$ (Howe's series) was prepared by three different methods. The details given by Howe are so very incomplete that much time was lost in working out the method of preparation in the following manner. Miolati's salt was first obtained by precipitating ruthenium trichloride in acid solution with potassium chloride. The precipitate (0·75 g.) was dissolved in 75 c.c. of water containing 1 c.c. of strong hydrochloric acid, 75 c.c. of absolute alcohol were added, and the solution was boiled under reflux for 20 minutes, when the colour changed from brown to light yellow. The alcohol was distilled off and the residual solution kept for a week. On evaporation, the salt $2K_2RuCl_5,3H_2O$ (Howe's series) separated in small, black crystals, which dissolved in water, giving a brown solution when concentrated and rose-coloured when very dilute [Found : Ru, 26·7; K, 20·3; Cl, 46·0; H_2O, 7·05 (by combustion). Calc., Ru, 26·5; K, 20·35; Cl, 46·1; H_2O, 7·0%].

(2) It appeared probable that the change from Miolati's series to Howe's series was caused by non-solvated hydrogen ions in accordance with the author's views of the catalytic activity of acids (Briggs, J., 1919, **115**, 278) and that the function of the alcohol was to increase the concentration of the non-solvated hydrogen ions. It was therefore expected that Howe's salt would be formed by boiling Miolati's salt with much acid in the absence of alcohol, and this was found to be the case. Owing, however, to partial oxidation by atmospheric oxygen the method is not suitable for preparing Howe's salt in quantity. A solution of Miolati's salt was boiled under reflux for 4 hours with strong hydrochloric acid

(2 vols.) and the resulting dark brown solution was evaporated to crystallisation. By repeated recrystallisation, the compound $2K_2RuCl_5,3H_2O$ was obtained in a pure condition [Found : Ru, 26·7; K, 20·4; Cl, 45·9; H_2O (diff.), 7·0%].

(3) The most convenient method for the preparation of the compound is by the action of alcohol and hydrochloric acid on a mixture of ruthenium trichloride and potassium chloride. Water (450 c.c.) containing 7 c.c. of strong hydrochloric acid, 450 c.c. of alcohol, 2·8 g. of ruthenium trichloride and 2 g. of potassium chloride was boiled under reflux for 20 minutes. The alcohol was distilled off and the solution was kept for a week, after which it was evaporated to crystallisation on the water-bath [Found : Ru, 26·6; K, 20·2; Cl, 46·1; H_2O (diff.), 7·1%].

If the solution is evaporated immediately after removal of the alcohol, impure products are obtained. For example, in one instance, a substance was formed which appeared to have the formula $K_2RuCl_5,2H_2O$ [Found : Ru, 26·0; K, 20·6; Cl, 45·1; H_2O (diff.), 8·2. Calc., Ru, 25·9; K, 19·9; Cl, 45·1; H_2O, 9·2%]. Several attempts to repeat the preparation of this substance were unsuccessful, but it is clear that more than one compound is present in the freshly-prepared solution.

When the preparation of Miolati's salt, K_2RuCl_5,H_2O, mentioned above, was treated with alcohol and hydrochloric acid, and the solution evaporated immediately after removal of the alcohol, the first crystals consisted of the compound $2K_2RuCl_5,3H_2O$ (Howe's series). The second crop, which was not quite homogeneous, gave Ru, 26·6; K, 21·0; Cl, 47·2; H_2O (diff.), 5·2. K_2RuCl_5,H_2O requires Ru, 27·1; K, 20·9; Cl, 47·3; H_2O, 4·7%. It is therefore possible that in Howe's series there is also a compound, K_2RuCl_5,H_2O, as originally described by Howe.

Oxidation of Howe's Salt by Air.—The compound $2K_2RuCl_5,3H_2O$ was dissolved in water and much hydrochloric acid was added. The solution was heated on the water-bath for several days and air was bubbled through, strong hydrochloric acid being added from time to time to make up the loss due to evaporation. A black, crystalline compound separated which was only sparingly soluble in water to give an intensely brown solution [Found : Ru, 27·6; K, 21·4; Cl, 48·3; H_2O (by combustion), 1·2, 1·1. K_2RuCl_5,K_2RuCl_5OH requires Ru, 27·8; K, 21·4; Cl, 48·5; H_2O, 1·2%]. Attempts were made to determine the valency of the ruthenium in this compound, but a suitable method for this purpose could not be devised.

Action of Chlorine on Howe's Salt.—(1) A 1% solution of the compound $2K_2RuCl_5,3H_2O$ became black when treated with chlorine. After prolonged passage of a current of chlorine, the black colour

disappeared, the solution becoming yellow with a strong odour of ruthenium tetroxide. The black solution gave a precipitate when strong electrolytes such as potassium chloride were added. The black colour was probably due to a colloidal substance, possibly ruthenium tetrahydroxide, which undergoes further oxidation to RuO_4. It should also be observed that, in the presence of very much acid, the compound $2K_2RuCl_5,3H_2O$ (Howe's series) is not blackened by chlorine or bromine.

(2) Chlorine was passed for 1½ hours through a cold solution of the salt $2K_2RuCl_5,3H_2O$ (Howe's series) (1·5 g.) in 15 c.c. of water, which was then evaporated in a vacuum over caustic potash and sulphuric acid to dryness. The residue of reddish-brown crystals and greenish-black scales was dissolved in hydrochloric acid and again evaporated in a vacuum to crystallisation. Only the reddish-brown crystals were now obtained [Found: K, 20·4; Ru, 26·65; Cl, 45·9; H_2O (diff.), 7·1. $2K_2RuCl_5,3H_2O$ (Miolati's series) requires K, 20·35; Ru, 26·5; Cl, 46·1; H_2O, 7·0%]. This salt in aqueous solution, unlike the corresponding compound in Howe's series, did not give a black coloration with bromine or chlorine. The colour of the very dilute solution was yellow.

(3) As Howe recommended treatment by chlorine in acid solution to prevent hydrolysis, the following attempt was made to prepare the compound K_2RuCl_6. The triaquodecachloro-dirutheniate, $2K_2RuCl_5,3H_2O$ (Howe's series) (8 g.) was dissolved in 27 c.c. of water and 1 c.c. of strong hydrochloric acid. After chlorination and evaporation, the black solution deposited 1·4 g. of a black, crystalline substance [Found: Ru, 26·7; K, 19·4; Cl, 44·3; $OH+H_2O$ (diff.), 9·6. Calc. for K_2RuCl_5OH,H_2O, Ru, 25·9; K, 19·9; Cl, 45·2; $OH+H_2O$, 8·9. Calc. for K_2RuCl_6, Ru, 25·9; K, 19·9; Cl, 54·2%]. On further evaporation of the solution, crystals of potassium chloride separated mixed with a further quantity of the black compound. The solution was filtered and the filtrate was evaporated to dryness and the residue dissolved in hydrochloric acid. On evaporation in a vacuum, brown crystals were deposited having the formula $2K_2RuCl_5,KRuCl_4,3H_2O$ or $K_5Ru_3Cl_{14},3H_2O$ [Found: Ru, 29·1; K, 18·7; Cl, 47·25; H_2O (diff.), 4·95. Required: Ru, 29·0; K, 18·6; Cl, 47·2; H_2O, 5·1%].

Note on Ruthenium Tetroxide.

The ruthenium tetroxide obtained by bubbling a current of chlorine through heated sodium rutheniate solution in a retort as described by Howe can be collected by means of an adapter dipping under water contained in a two-necked Woulfe's bottle, a delivery tube from the second neck taking the fumes into an absorption

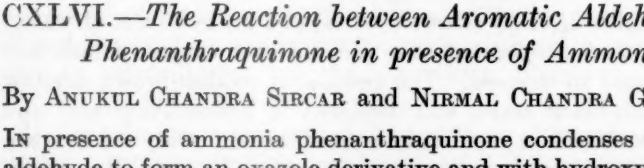
apparatus filled with aqueous alcoholic potash. The ruthenium tetroxide falls to the bottom of the bottle as a yellow solid which dissolves completely after standing some hours and the solution can then be reduced by pouring into aqueous potash containing alcohol. This method of working is very much more convenient than the method used by Howe.

[*Received, December 9th*, 1924.]

CXLVI.—*The Reaction between Aromatic Aldehydes and Phenanthraquinone in presence of Ammonia.*

By Anukul Chandra Sircar and Nirmal Chandra Guha Ray.

In presence of ammonia phenanthraquinone condenses with benzaldehyde to form an oxazole derivative and with hydroxy-aldehydes to form iminazoles (Japp and Wilcock, J., 1880, **37**, 661; 1881, **39**, 225; Japp and Streatfeild, J., 1882, **41**, 146):



Aromatic nitro- and bromohydroxy-aldehydes also yield iminazoles (Sircar and Sircar, J., 1923, **123**, 1559).

When the reaction was applied to acenaphthenequinone, oxazoles were sometimes formed instead of the expected iminazoles (unpublished work). This result led to a study of the action of aromatic aldehydes on phenanthraquinone in presence of ammonia under various conditions and it was found that, although the exact conditions are different for each aldehyde, in general one and the same aldehyde gives an oxazole at a low temperature and an iminazole at a high temperature. The course of the reaction, therefore, is not dependent on the nature of the aldehyde, as was suggested by Japp and Streatfeild (*loc. cit.*).

2-*Phenylphenanthriminazole.*—The product obtained by heating 1 g. of phenanthraquinone, 1 g. of benzaldehyde, and 25 c.c. of strong aqueous ammonia at 160—170° for 4 hours was finely powdered and digested with boiling benzene. The residue crystallised from pyridine in clusters of light yellow needles, not melting below 295°. It was readily soluble in pyridine, nitrobenzene, acetic acid, acetone, or alcohol, slightly soluble in benzene, and produced a blue solution with concentrated sulphuric acid (Found: N, 9·8. $C_{21}H_{14}N_2$ requires N, 9·5%).

2'-Hydroxy-2-phenylphenanthroxazole.—A solution of 1 g. of phenanthraquinone and 1·2 g. of salicylaldehyde in 250 c.c. of warm amyl alcohol was cooled to 10—15° and treated with dry ammonia gas for 15 minutes, the quinone, which had separated on cooling, soon dissolving. The solution was immediately concentrated; the precipitate obtained crystallised from pyridine in colourless needles, m. p. 231—233°. The oxazole is readily soluble in pyridine, nitrobenzene, or acetone, slightly soluble in acetic acid or benzene, insoluble in alcohol, and develops a bluish-green fluorescence with strong sulphuric acid (Found: N, 4·9. $C_{21}H_{13}O_2N$ requires N, 4·5%).

3'-Nitro-2-phenylphenanthroxazole, prepared in the same way as the preceding compound (dry ammonia gas was passed for 20 minutes) from phenanthraquinone (1 g.) and *m*-nitrobenzaldehyde (1·2 g.), crystallised from pyridine in light yellow needles, m. p. 248°. It was insoluble in acetone, slightly soluble in acetic acid, benzene, or alcohol, and readily soluble in pyridine or nitrobenzene. With strong sulphuric acid it developed a greenish-yellow coloration (Found: N, 8·7. $C_{21}H_{12}O_3N_2$ requires N, 8·2%).

2'-Nitro-2-phenylphenanthroxazole, prepared in a similar way from *o*-nitrobenzaldehyde, separated from pyridine in yellow needles, m. p. 166°. It was slightly soluble in alcohol or acetone, soluble in pyridine, nitrobenzene, acetic acid, or benzene, and dissolved in concentrated sulphuric acid with a yellowish-brown colour (Found: N, 8·5. $C_{21}H_{12}O_3N_2$ requires N, 8·2%).

2'-Nitro-2-phenylphenanthriminazole, obtained in the same way as 2-phenylphenanthriminazole (*vide supra*) from *o*-nitrobenzaldehyde (1·2 g.) and phenanthraquinone (1 g.), crystallised from nitrobenzene in light yellow, hexagonal plates.

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CXLVII.—*The Measurement of the Dielectric Constants of Liquids.*

By HERBERT HARRIS.

AN attempt to correlate on a physico-chemical basis certain electrolytic phenomena with the dielectric constants of liquids led to the work embodied in this paper. The existing methods of determining the dielectric constants at telephonic frequencies are open to considerable objection, and the aim of the present paper is to discuss critically and explore experimentally the measurement of the dielectric constants of liquids by alternating current bridge methods.

Methods of Measurement.—The three main methods of determin-

ing the dielectric constants of liquids are : (*a*) the method which depends upon the frequency of oscillation of a triode valve circuit (Graffunder, *Ann. Phys.*, 1923, **70**, 225; Herweg, *Verh. deut. Phys. Ges.*, 1919, **21**, 272; Grützmacher, *Z. Physik*, 1924, **28**, 342). This method, however, is sensitive only at frequencies of the order of 10^5 to 10^6 cycles per second; (*b*) the wave-length method, developed by Drude and used extensively by Walden. Some limitations and possibilities of this method have been discussed by Southworth (*Phys. Rev.*, 1924, **23**, 631); (*c*) alternating current bridge methods, which are the most suitable for telephonic frequencies of 350 to 5000 cycles per second.

The third method is the one which has been used in the present work. In the published papers on the dielectric constants of liquids, of interest to chemists, there is little real understanding of measurements of this kind. It is proposed, therefore, first of all to discuss critically, with due regard to the special difficulties arising in the case of liquids which are not insulators, the alternating current bridge methods which may be employed. For good insulators, the methods are adequately dealt with in several standard works, particularly in Hague's "Alternating Current Bridge Methods," which became available while this investigation was in progress.

Before a proper understanding of the principles underlying bridge methods can be obtained, two points must be carefully considered :—

(i) *The equivalent circuit of an imperfect condenser.* When an alternating current is applied to a perfect condenser, the current vector leads by 90° on the voltage vector. With an imperfect condenser, the angle of lead is reduced by some angle θ, known as the "*loss angle*," which may be taken as a measure of the imperfection. It may vary from a few seconds in the case of a good laboratory standard condenser to nearly 90° in the case of "condensers" with certain liquids as dielectric.

To balance an imperfect condenser, either of the two systems A and B (Fig. 1), composed of perfect condensers K and C and pure resistances R and S, may be adopted. The only object of the resistances is to give the same phase displacement as the imperfect condenser by dissipating, as heat, the same amount of power. It can readily be shown (compare Hartshorn, *J. Brit. Elect. Manuf. Assoc.*, 1923, **13**, 89) that when these two systems are each equivalent to the imperfect condenser, with loss angle θ,

$$\cos^2\theta = C/K.$$

It is to be noticed that $C \neq K$ unless $\cos^2\theta = 1$, that is, unless θ is negligibly small. Therefore the capacity of a condenser, with an appreciable loss angle, possesses two values, which, apparently, have exactly similar claims to being regarded as correct. Since, however,

the capacity determined by the parallel resistance method yields values of the dielectric constant in agreement with values determined by other methods, it is natural to give preference to this system of measurement.

(ii) *Earth capacities.* In defining the capacity of a simple condenser the influence of neighbouring bodies is usually neglected. It is of practical importance to analyse the capacity distribution when more than two conductors are involved.

In the case of a shielded air condenser, having a pair of electrodes insulated from and surrounded by an earthed metallic screen, as in Fig. 2A, it can be shown that

$$C = C_{12} + C_1C_2/(C_1 + C_2)$$

where C is the apparent capacity between the electrodes, C_{12} is the intercapacity between the electrodes, and C_1 and C_2 are the earth capacities of the two electrodes (compare Fig. 2B) (for details, see Hague, *op. cit.*, or "Dictionary of Applied Physics," edited by Glazebrook, 1924, Vol. II., p. 103).

The special importance of the above analysis arises from the fact that, by introducing a liquid (D.C. $= \epsilon$) as dielectric, it will not always be possible to write the new capacity, C', of the condenser as $C' = \epsilon C$; it may be more accurate to write

$$C' = \epsilon C_{12} + C_1C_2/(C_1 + C_2)$$

or C_1 and C_2 may be slightly affected; the change will depend upon the geometrical arrangement of the conductors.

Thus, in the bridge set-up, special attention must be directed to the design of the condenser, and also to the method by which it is inserted in the bridge.

Series Resistance Method.—Apparently the simplest method of determining capacity is by the bridge introduced by De Sauty and applied to alternating current measurements by Wien (*Ann. Physik*, 1891, **44**, 697). In practice, however, the bridge is almost useless, because sharp balance cannot be attained, no measures being adopted to balance the imperfections of the condenser.

Modifications of the De Sauty method have therefore been adopted to neutralise the condenser leaks. In one of the simplest, a variable resistance is placed in series with the condenser with the smaller loss angle; but it is of little importance when dealing with liquids which behave as poor dielectrics, such as chloroform, nitrobenzene, acetone, etc. For example, in the case of chloroform, θ is of the order of $24\frac{1}{2}°$; if C (refer to system B, Fig. 1) $= 0{,}00100$ microfarad, then $K = 0{,}00152$ microfarad. Again, for commercial acetone, with $\theta = ca.\ 89\frac{1}{2}°$, and $C = 0{,}00100$, $K = 13$ microfarads, which would be an absurd value to take, because it would correspond to a dielectric constant of approximately 260,000.

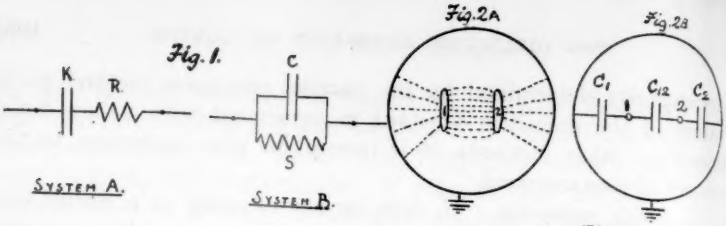
Fig. 1.
K
R
C
S
SYSTEM A.
SYSTEM B.
Fig. 2A
Fig. 2B
C1
C12
C2
1
2

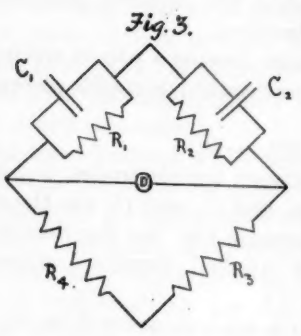
Fig. 3.
C1
C2
R1
R2
R4
R3

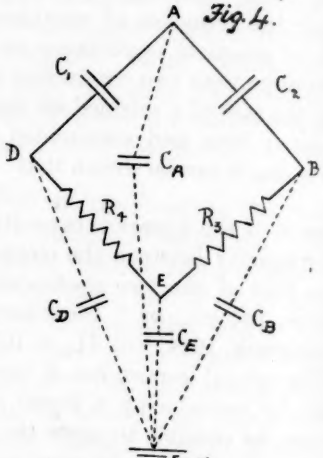
Fig. 4.
A
C1
C2
D
CA
B
R4
R3
E
CD
CE
CB

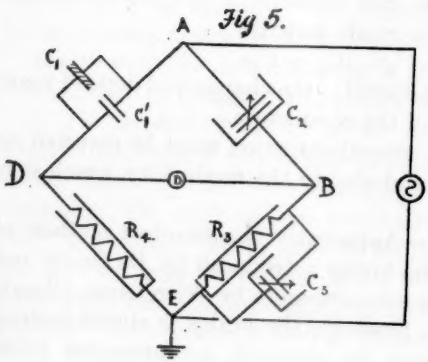
Fig 5.
A
C1
C'1
C2
D
B
R4
R3
E
C3

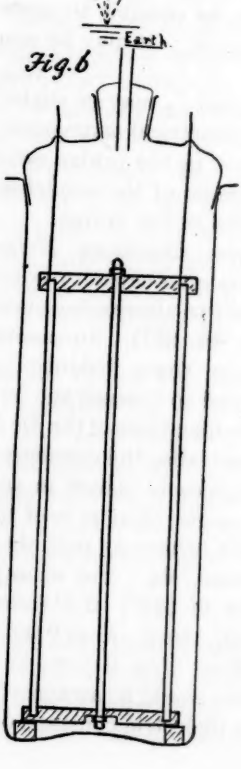
Fig. 6
Earth

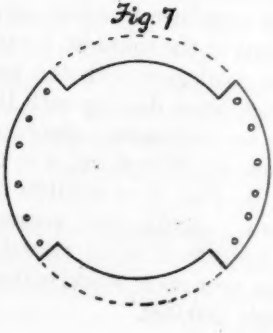
Fig. 7

It is realised immediately that this method is restricted to liquids with very high insulating powers, such as benzene and carbon tetrachloride, in which cases very satisfactory results may be obtained.

Parallel Resistance Method.—This is the method most frequently used, and is easily understood by reference to Fig. 3; the condenser leak is balanced by a resistance in parallel with the standard condenser.

This method is the only one possible when the dielectric possesses a large loss angle, for instance, chloroform, ethylene dichloride, etc. With good dielectrics the method can still be used, but in order to overcome the difficulty of using very high resistances in parallel with the standard condenser, both condensers have to be shunted by suitable resistances. But this plan is not to be recommended because, by so doing, an appreciable quantity of the current passes through the resistances, thus reducing the sensitivity of the condenser setting.

The series resistance method, therefore, is the better when dealing with dielectrics characterised by small loss angles, and the parallel resistance method is used when the loss angle increases. The limit of the method is determined by the sensitivity of the condenser setting.

Earth Capacities; Their Effect on the Bridge.—Before passing to the description of the Schering and Semm's bridge, it will be convenient to discuss the effects of earth capacities on the bridge.

As is well known, every portion of a conductor has a capacity to earth, so that in any bridge set-up this capacity is distributed continuously along every arm. Giebe, however, has shown that, to a near approximation, the total effect of this distribution can be represented by four capacities from the four corners of the bridge to earth, represented in Fig. 4 by the dotted construction. This approximation is not justified in the case of bridges where the arms contain such things as high resistances, in which there are distributed capacities of considerable magnitude.

From the figure, it is clear that the arm AD is not composed solely of the condenser C_1, but C_1 and a combination of C_A and C_D. Actually the capacity of the arm can be written as $C_1 + C_A C_D/(C_A + C_D)$. Similarly, the effective capacity of the arm AB is $C_2 + C_A C_B/(C_A + C_B)$, the impedance of the arm DE is $1/\{1/R_4 + jwC_D C_E/(C_D + C_E)\}$, and the impedance of the arm BE is $1/\{1/R_3 + jwC_B C_E/(C_B + C_E)\}$. Therefore, the impedances of the arms have to be corrected for these earth capacities.

There is also a further effect due to earth capacities. In the bridge, a telephone is placed across the points D and B. Now the observer being at earth potential and D and B being at some other potential, there will be a leak from the bridge, through the observer, to earth,

giving rise to what is known as the "head effect" of the observer. These difficulties can be overcome very ingeniously by Wagner's earthing device (*Elektr. Z.*, 1911, **32**, 1001; 1912, **33**, 635). A detailed description is given by Hartshorn (*loc. cit.*) and by Hague (*op. cit.*).

The use of the Wagner earthing device would make the measurements very much more difficult. It is quite difficult to obtain a well-defined minimum when only one arm has to be adjusted, and if it were necessary to balance a subsidiary arm and then the bridge arm, and repeat this process until satisfactory balance is obtained for both arms, the time so spent would be sufficient for the power, dissipated as heat in the experimental condenser, to cause a marked rise in the temperature of the dielectric. The difficulty has therefore been overcome by using the device of Monash (see later), which, though not so sound theoretically, offers, in this case, considerable practical advantages over the arrangement of Wagner.

Schering and Semm's Bridge.—This method, suggested by Schering (*Z. Instrum.*, 1920, **40**, 124), and actually first used by Semm (*Arch. Elektr.*, 1920, **9**, 30), was primarily designed for high voltage work, but Giebe and Zickner (*ibid.*, 1922, **11**, 109) have used it in an exceedingly accurate investigation, in which they measured the loss angles of standard condensers (of the order of 1″) (see also Hartshorn, *Proc. Physical Soc.*, 1924, **36**, 399).

The method is limited in application to liquids which possess a fairly small loss angle, but for such liquids (benzene, carbon tetrachloride, etc.) it is by far the most satisfactory.

The principle of the method is illustrated by Fig. 5. The shaded condenser, C_1, is the one to be measured; its capacity is measured on the condenser C_2, the ratio arms being the resistances R_3 and R_4.

Before perfect balance is obtained in any alternating current bridge not only must the two detector terminals be at the same potential, but the voltages at the two points must also be in phase. In all the bridges previously dealt with, the phase difference has been rectified by a resistance in parallel, or in series with the standard condenser. In Schering and Semm's bridge, this has been accomplished by placing a variable condenser across the resistance R_3. It can be shown that when such a bridge is balanced, $\rho_1 = C_3/C_2 \cdot R_4$ (where ρ_1 is the equivalent series resistance of condenser C_1) and $C_1/C_2 = R_3/R_4$.

A second point is to be noted. One sees that the point E is earthed. Now the resistances R_3 and R_4 are made very small—in these experiments 1000-ohm coils are used—the result, therefore, is that the drop in potential across the resistances is only a small fraction of the drop across the condensers (whose impedance is approximately 150,000 ohms). Therefore the potentials at the

points D and B are nearly at earth value, and thus the effect of earth capacities in the bridge and the head effect are eliminated. This device due to Monash (*Electrician*, 1907, **59**, 416, 460, 504), was used in all the experiments in this investigation, even when the parallel resistance method was employed.

The method of shielding the apparatus from outside disturbances, to which particular attention must be paid, is indicated in the figure. The aim has been to maintain every screen at or near earth potential; thus the two screens shielding the resistances are directly earthed and the condenser screen is connected to the point B, which, as has been said, is nearly at earth potential.

Since, in general, the rotating plates of the condenser are connected to the screen, it is obvious that the method of screening adopted tends to reduce the effect of the hand capacity when the condenser is adjusted by hand. As a matter of fact, a bridge so screened is very insensitive to outside capacities.

The construction of the experimental condenser will be discussed later.

Apparatus.—The generator. The development of the triode valve has resulted in a valve generator which is entirely satisfactory for the purpose in hand. The valve generator was made by the Cambridge and Paul Company, and has the following features:—(1) It supplies a pure sine-wave current of constant frequency. (2) Its frequency can be adjusted to any value between 50 and 5000 cycles per second by altering the value of the capacity unit. (3) It requires little attention. (4) One set of windings is suitable for high impedance bridges. (5) Between the primary and secondary windings there is a screen, which by connecting to earth prevents direct interference of the generator on the bridge.

The frequency of the generator was calibrated against two König tuning forks (frequencies 1024 and 2048). The frequency was given by the formula $n = a/\sqrt{C}$, where a is a constant and C the value of the capacity unit.

Another tuning fork, frequency about 890, was then calibrated against the generator, and its frequency thus determined served as a test of the generator frequency from week to week. Little variation was observed. In every experiment the generator was adjusted so that it gave a frequency of 1000 cycles per second.

The detector. The necessity for an accurate setting of the frequency of the generator is to ensure maximum sensitivity being obtained. Since a telephone (made by Brown) sensitive at 1000 cycles per second was used as detector and since in the sensitivity–frequency curve for a telephone of this description there is a very sharp peak, it becomes evident why strict attention was paid to this point. It

may be taken as a general rule that a given telephone is at least three times as sensitive at its resonance frequency as at any other.

There is one other point to be noted about the detector: for maximum sensitivity, a high impedance bridge requires a high impedance detector. It was accordingly found that a 1000-ohm telephone was far more sensitive than a similar 120-ohm one, and the former was therefore used.

The ratio arms. It has been seen that, in general, the ratio arms are two resistances. In the Fleming and Dyke bridge, two condensers are used. The advantage of this method is that it is fairly easy to construct the condensers with small residuals, whereas with large resistances the residuals become important. Nernst and his co-workers (Nernst, *Z. physikal. Chem.*, 1894, **14**, 622; Philip, *ibid.*, 1897, **24**, 18; Turner, *ibid.*, 1900, **35**, 385), together with many recent workers in this field, have used liquid resistances, mannitol–boric acid solution. Two points are to be noted regarding such resistances. The platinum electrodes must be thickly platinised, so as to reduce to a minimum their residual capacity, due, for instance, to polarisation capacity. On the second point, I wish merely to state my own experience, namely, that it was not found possible to maintain constant the ratio of the two resistances, constructed according to Turner's directions.

It must nevertheless be conceded that the introduction by Nernst of liquid resistances of, say, 20,000 ohms with very small residual capacity, possibly one or two micro-microfarads, was an immense improvement on the large coils of wire, with large residuals, that would otherwise have been needed.

Since, however, in these experiments only comparatively small resistances were required, the ratio arms were specially obtained. They were two 1000-ohm coils, guaranteed to within 0·02% ohmic accuracy, made by H. W. Sullivan. They are the so-called non-reactive coils, possessing very small residuals; they are further guaranteed to be equal to each other with an accuracy of 0·01%.

The standard condenser. Undoubtedly the most important portion of the bridge is the measuring instrument, that is, the standard condenser. This condenser should have the following properties:— (1) it should be a true condenser, that is, the current taken by it when a sinusoidal potential difference is applied should lead on the potential difference by $\pi/2$ and should be free from harmonics; (2) it should be free from losses and absorption effects in the dielectric; (3) the capacity should be definite and permanent; (4) the capacity should be independent of the frequency, wave-form, and temperature.

Given this set of conditions, it is possible to use only air or mica

as the dielectric material. "Other materials are only used where capacitance is required without the advantages of permanence, accuracy, and perfection" (Hague, *op. cit.*).

The condenser used in this investigation was a laboratory standard air condenser, made by H. W. Sullivan, and fitted with a vernier and lens. The maximum capacity was about 1200 $\mu\mu$f., and the scale was divided into degrees, being read to 0·1° by means of the vernier. 0·1°, or 1 unit, was equal to 0·700 $\mu\mu$f. In this paper, all the capacities are quoted in these units, unless otherwise stated. Thus a capacity of 100 will mean a capacity of $100 \times 0{\cdot}700\ \mu\mu\text{f.} = 70\ \mu\mu\text{f.}$

The calibration of the condenser was furnished by the maker, and over the range used the capacity was a linear function of the scale reading.

With the bridge correctly balanced, the condenser can be set to less than 0·700 $\mu\mu$f. Indeed, with such liquids as benzene, an enlarged scale would certainly be an advantage, because the setting of the condenser is so well defined. There would be little difficulty in setting the bridge to within 0·1 $\mu\mu$f. with a capacity of 1000 $\mu\mu$f.

Criticism of the Nernst Method.—A considerable amount of time was initially spent with a bridge constructed from apparatus of the Nernst-Turner type. In view of the importance attached by chemists to Turner's investigation (see, *e.g.*, Richards and Shipley, *J. Amer. Chem. Soc.*, 1919, **41**, 2002), it may be of value to subject it to a critical examination, for in the author's judgment the accuracy of the method is open to question.

(1) Apart from the fact that the Nernst interrupter does not meet modern requirements, the Nernst-Turner type of condenser, which has been used by many workers (see, *e.g.*, Hertwig, *Ann. Physik*, 1913, **42**, 1099; Joachim, *ibid.*, 1919, **60**, 570; Harrington, *Physical Rev.*, 1916, **8**, 581; Richards and Shipley, *loc. cit.*), does not behave as a true condenser, *i.e.*, the current does not lead on the voltage by $\pi/2$ when a sinusoidal potential difference is applied. This must be so, because glass possesses a relatively large loss angle, and when the condenser is balanced against a perfect condenser an appreciable resistance must be used to rectify the phase displacement. With the Schering and Semm's bridge, used in these experiments, the maximum value of the condenser C_3 (Fig. 5) is 0·001 microfarad, and the resistances are 1000 ohms each. With this bridge it is not possible to balance the Nernst-Turner condenser, although with the same arrangement a benzene condenser of at least twice the capacity has been accurately balanced. From this observation it follows that, if the dielectric constant of benzene were being determined by the method of Turner, *the measuring condenser would have a much greater loss angle than the condenser to be measured.*

Further, Thornton (*Proc. Physical. Soc.*, 1912, **24**, 301), studying the behaviour of dielectrics, when placed in an alternating current field, by means of an oscillograph, has shown that glass is not only an imperfect dielectric in so far as it reduces the current lead, but also distorts the current wave. In such a case, it is impossible to find any combination of a perfect condenser and a resistance which will produce the same effect. This means that, when used in a bridge, the glass condenser cannot be accurately balanced.

(2) The capacity of the condenser cannot be said to be definite and permanent. The condenser permits of slight lateral displacements involving changes of capacity without change of the scale reading.

(3) The capacity cannot be taken as independent of the temperature, and of this Turner was aware, because he made special determinations of the temperature coefficient of his apparatus.

(4) Further, the use of the Nernst-Turner condenser involves the sliding of the glass plates between the brass plates, and during the process the dust particles that inevitably collect on the top edges of the glass plates form a ridge across the brass plates and thus create a shunt across the condenser, greatly increasing the loss angle. If this minute ridge is brushed away, one notices a distinct improvement in the loss angle.

(5) In the Nernst method electrolytic resistances, consisting of platinum electrodes in Magnanini's solution, are employed. The author found it impossible to maintain their resistance ratio constant, even although the special advantage of Magnanini's solution is that its resistance possesses a small temperature coefficient.

In the following tables are set out the results of experiments in which the two resistances formed two arms of a bridge, a Leeds and Northrup conductivity bridge wire (drum type) forming the other two arms.

Resistances about 2,000 ohms.

Time (mins.).	Temp. of room.	Bridge reading.	Ratio of the two resistances.
0	9·7°	497·15	0·9887
15	10·05	498·2	0·9928
30	10·7	498·9	0·9956
45	10·9	499·5	0·9980
60	11·5	500·2	1·0008

Resistances about 15,000 ohms.

Time (hrs.).	Bridge reading.	Ratio of the two resistances.
0	496·6	1·0137
½	496·6	1·0137
1¼	496·5	1·0141
2¼	496·4	1·0145
3¼	496·4	1·0145
8¾	497·5	1·0101
24¾	498·3	1·0068
—	498·2	1·0072
32¾	498·0	1·0080
36¼	497·6	1·0090
38¼	497·5	1·0101

With such resistances it is not possible to obtain very accurate results and therefore they were discarded.

(6) In Turner's investigation no attention seems to have been

paid to the influence of earth capacities on the bridge. Such effects were very marked, for it is stated that slight movements of the observer caused an appreciable shift in the position of balance, and Turner insists on the observer maintaining a constant position with respect to the apparatus. This, in itself, is proof that large earth capacities were affecting the bridge. In a bridge of the type used, the only method of successfully ensuring the correctness of the minima is to use a Wagner earthing device.

It might be noted, too, that Turner, in some of his experiments, placed his dielectric trough in a massive piece of brass, in order to reduce any temperature variations. This seems to be open to criticism, because the earth capacity of the metal must have quite a considerable value.

Description of the Bridge Set-up.

(*a*) *Direct action between the generator and the bridge and the telephone.* The valve generator was placed about 6 feet from the bridge itself and about 14 feet from the telephone. At these distances there was no direct inductive action between the generator and the bridge, and no capacity effects were introduced, because reversal of the connexions to the generator caused no change in the balance point. The action of the generator on the telephone was very small, reversal of the telephone connexions causing only a negligible change in the reading.

(*b*) *Loose connexions in the bridge.* The connexions at the points D, B and A (Fig. 5) were made with mercury cups in ebonite, screwed to the bench. All bad contacts were thus eliminated, and, since the bridge was symmetrical with respect to the cups, no unbalanced capacity was introduced.

(*c*) *The insulation of the bridge* received particular attention. All the apparatus which was not provided with screens, *e.g.*, the leads, was supported on ebonite stands about 2 inches from the bench. Such insulation is of particular importance in all high impedance bridges.

(*d*) *The condenser* C_3, made by Gambrell, had a maximum capacity of 0·001 microfarad. The condenser C_1' was a small Murdoch condenser, maximum capacity 0·0005 microfarad, which was set so that the "zero" of all readings on the standard condenser was a point on the "straight line portion" of its capacity. The capacity to be measured was inserted across this small condenser and the increase in capacity was the capacity required.

(*e*) *Correction due to the capacity of the leads.* The two leads which connect the experimental condenser to the bridge cannot be balanced by "dummy" leads. Thus a small correction has to be applied to the value of the capacity as above measured. This correction

is obtained by noting the increase in capacity when the container of the experimental condenser and the leads, but minus the condenser itself, are inserted in the bridge. This correction was about 1·5 units or about 1$\mu\mu$f. and was determined for every container used.

(*f*) *Earth capacity and motion of the observer.* The movement of the observer had very little effect on the position of the bridge setting. This was taken to be substantial evidence that the bridge was well screened and that errors due to earth capacities were negligible. But in every case the observer was 6 feet or so from the bridge, the condenser being operated by a long wooden arm from that distance.

(*g*) *The insertion of the experimental condenser.* As will be seen later, the experimental condensers consisted of two concentric metal cylinders contained in a glass vessel. The point here emphasised is that the outer cylinder is connected to the point D of the bridge and the inner cylinder to the point A. The outer cylinder, which also serves as a screen to the inner one, is thus connected to a point practically at earth potential, so that the working capacity of the condenser is actually the capacity between the two plates, that is, C_{12}.

(*h*) *Temperature control.* The experimental condenser was placed in an electrically heated and controlled thermostat, which maintained the temperature at 25·00° with a variation of less than 0·01°. Whenever a reading was being taken, the electric heater was disconnected from the supply main.

(*i*) *Correction due to the capacity of the parallel resistance.* In the case of liquids with large loss angles, where the use of Schering and Semm's bridge was not possible, the condenser C_3 (Fig. 5) was removed by disconnecting from the bridge, at B, and earthing both terminals, and the parallel resistance method was employed. The liquid resistances were similar to those used by Turner, being varied by the movement of conical plungers. In these experiments, a resistance has to be inserted across the measuring condenser to balance the imperfections of the experimental condenser. This resistance must obviously have a small residual capacity, which must be corrected. For this purpose, the resistance is placed in the opposite side of the bridge and the bridge is balanced by means of a second similar resistance. The first resistance is then removed, and the bridge again balanced. The difference in the two capacity settings, which is generally of the order of 3 or 4 micro-microfarads, may be taken as the residual capacity of the resistance. The only assumption made in this method of correction is that the residual capacity of the second resistance does not vary when the plunger is moved.

This method has been adopted in preference to putting two resistances (permanently) in opposite arms of the bridge, as is

so frequently done, because in the method adopted one gets the maximum sensitivity obtainable.

(*j*) *Schering and Semm's bridge for zero balance.* In the large number of cases where the parallel resistance method was used, the zero setting of the bridge would have been troublesome because, the small Murdoch condenser C_1' having a much larger loss angle than the measuring condenser, perfect balance would not have been immediately attainable. To obtain such a balance readily, Schering and Semm's bridge, involving the use of the condenser C_3, was employed and when the zero setting had been obtained the condenser C_3 was again earthed. This is a considerable improvement on previous methods of working.

(*k*) *The minima.* In all the experiments exceptionally good minima were obtained, the telephone being quite silent. For good work, perfect quietness is essential.

(*l*) All the results have been calculated on the assumption that polarisation capacities in the experimental condenser are absent. It is an assumption always made in this type of work, but it could only be proved by experiment.

The Experimental Condensers.—A series of condensers was constructed so that maximum accuracy could be secured. If the maximum capacity that can be measured is 1200 $\mu\mu$f., a condenser containing nitrobenzene as dielectric must have an air capacity of about $1200/35 = 35\,\mu\mu$f., and with benzene as dielectric, a capacity of about 70 $\mu\mu$f. Since the dielectric constant of nitrobenzene is the ratio of two capacities, if nitrobenzene is standardised against benzene, the experimental value $2 \times 1200/70$ will be obtained. The accuracy of this expression, being determined by that with which the capacity 70 $\mu\mu$f. is measured, is poor. It is clear, therefore, that a standard series of liquids with increasing dielectric constant must be obtained in order that any condenser may be accurately standardised. The method adopted was to measure the dielectric constant of benzene against air, that of chloroform against benzene, that of ethylene dichloride against chloroform, and so on, the smallest capacity measured thus being 400 $\mu\mu$f.

The requisite condensers were all constructed on the following principle. Two concentric brass cylinders were supported in compressed fibre end-pieces, grooved to take the cylinders at a "push fit." The end-pieces were bolted together as indicated in Fig. 6, and the whole was placed on a fibre ring in a stoppered glass container. The leads were soldered to platinum wires, which were sealed through the stopper and were there soldered to the leads to the bridge. Through an orifice in the stopper the liquid was poured in when the condenser was assembled. The stopper of the orifice was provided with a tube and tap (not shown in the figure), by which

the condenser vessel could be evacuated and any air bubbles trapped between the condenser plates removed. To facilitate this removal small holes were bored through the fibre end-pieces so that the space between the condenser plates had direct communication with the outer space. The dimensions will be given later.

Method of Calculating the Dielectric Constant.

In all the measurements recorded in this work, a correction has to be applied for that portion of the capacity of the condenser which is influenced by the fibre end-pieces.

With air as dielectric, the capacity, measured across the terminals of the two condenser leads, is composed of two parts, *viz.*, that due to air as dielectric, x, and that caused by the fibre end-pieces, y. If a liquid, say, benzene, is introduced, the capacity is still composed of two parts, *viz.*, that due to benzene as dielectric, ϵx (where ϵ is the dielectric constant of benzene), and y. It would thus appear that a constant quantity, y, has been added to the two capacities whose ratio gives the dielectric constant of benzene. Thus are obtained the two equations

$$x + y = a \text{ and } \epsilon x + y = b,$$

where a and b are determined experimentally.

After these readings have been taken, the fibre end-pieces can be cut (as shown in Fig. 7) so that they cover only half the rim of the condenser, the capacity due to the fibre end-pieces thus being exactly halved. With this new condenser, two equations are again obtained,

$$x' + \tfrac{1}{2}y = c \text{ and } \epsilon x' + \tfrac{1}{2}y = d,$$

where x' is the value corresponding to x, for the second condenser. From these four equations, the four unknown quantities x, y, x', and ϵ can be determined.

A little thought, however, will show that this view is not quite correct. The objection is, that y is not constant.

With air as dielectric (D.C. = 1), there will be a certain crowding of the lines of force into the fibre end-pieces (D.C. = 3·5), giving rise to the capacity due to the end-pieces. When benzene is used as dielectric, there will not be the same crowding of the lines of force at the interface between the fibre and the dielectric, because the difference in the two values of the dielectric constants is not so great as previously, and therefore the capacity of the end-pieces is somewhat reduced.

The method of attack adopted is somewhat arbitrary, but the result was tested in the case of benzene and was found to be satisfactory. With the full end-pieces on the condenser, the ratio of the capacities of the condenser, measured in air and in benzene, is z_1. With half the end-pieces, this ratio is slightly increased to a value z_2.

It is assumed that if the remaining halves of the end-pieces could be removed, the second increase in the ratio would be the same as the first. The dielectric constant of benzene is therefore calculated as

$$z_1 + 2(z_2 - z_1) \text{ or } z_2 + (z_2 - z_1).$$

Justification for this procedure was obtained experimentally. A new condenser was constructed exactly similar to the first except that its length was reduced to a quarter of the previous value, and its air capacity was measured. Subtraction of this capacity from the air capacity of the larger condenser gives the capacity, due to air as dielectric, of a "virtual condenser" without any end interference. This being repeated with benzene as dielectric in the two cases, the difference now gives the capacity of the same "virtual condenser" with benzene as its dielectric. The ratio of these two quantities must be the true dielectric constant of benzene.

For benzene, the two methods gave the same value for the dielectric constant, *viz.*, $2{\cdot}2482 \pm 0{\cdot}0003$ and $2{\cdot}2488 \pm 0{\cdot}0005$.

The probable errors of the means (see Tables) have been calculated by the method of "least squares." The author is aware that a detailed analysis of the results would show inconsistencies, but wishes the probable errors given to be taken as indicating the order of accuracy of the final results.

Purification of Materials.

Benzene. Commercial benzene was shaken successively with concentrated sulphuric acid, water, and distilled mercury to remove thiophen, sulphuric acid, and any sulphur compounds respectively. The filtered liquid was washed with water, dried over calcium chloride, fractionally distilled, and thoroughly dried over sodium wire (Richards and Shipley, *J. Amer. Chem. Soc.*, 1914, **36**, 1825; 1919, **41**, 2002). It distilled within a range of 0·02°.

Carbon tetrachloride, obtained from the British Drug Houses, was dried with calcium chloride and fractionally distilled, the bulk passing over within a range of less than 0·1°.

Chloroform (A.R.) was shaken once with sodium bisulphite solution, twice with water, and thrice with concentrated sulphuric acid. After being thoroughly washed with water, it was dried over calcium chloride and fractionally distilled through a moderately efficient column (Richards and Camm, *J. Amer. Chem. Soc.*, 1921, **43**, 827; Schoorl and Regenbogen, *Rec. trav. chim.*, 1922, **41**, 1). The b. p. of the resultant fraction was constant to within 0·03°. If carbonyl chloride is formed by the action of light, it is readily detected by the change in the odour of the chloroform, and may be removed by shaking with solid sodium hydroxide. To ensure uniformity of the chloroform samples used throughout the lengthy series of experi-

ments, every sample was tested, the criterion of uniformity or purity being the refractive index. The values of $n_D^{25°}$ observed for the several samples were 1·4433, 1·4433, 1·44326, 1·44321, 1·44329, 1·44327, 1·44319, 1·44331.

Ethylene dichloride, obtained from the British Drug Houses, was shaken with concentrated sulphuric acid and with water, and then with potassium hydroxide for 2 days. It was again washed with water, dried over calcium chloride, and fractionally distilled through an efficient Young's column (Worley, J., 1914, **105**, 273; Timmermans, *Bull. Soc. Chim. Belg.*, **1910**, **24**, 246). After three distillations, there was no improvement in the b. p. (83·0—83·3°) or refractive index. The values of $n_D^{25°}$ of the several samples were 1·44197, 1·44205, 1·44211, 1·44211, 1·44215.

o-*Nitrotoluene* (Kahlbaum) was distilled several times under reduced pressure, the first and last fractions being rejected. It was then dried by shaking with phosphorus pentoxide for 30 hours, and after filtration was twice distilled under reduced pressure (25 mm.). Moisture appears to have a large effect on the dielectric constant. The values of $n_D^{25°}$ for the several samples used were 1·54418, 1·54442, 1·54421.

Nitrobenzene (purified) was left standing for several days with bromine. The bromine was then removed with dilute caustic soda solution, and the nitrobenzene washed with water, dried over calcium chloride, and distilled. The middle fraction, comprising more than 90% of the whole, remained unchanged in b. p. (range within 0·1°) and refractive index ($n_D^{25°}$ 1·55006) after several redistillations. It was then shaken for several days with freshly prepared silver oxide (dried at the ordinary temperature), dried over phosphoric oxide, and distilled under about 20 mm. pressure (Bruner and Galecki, *Z. physikal. Chem.*, 1913, **84**, 513).

TABLE I.

Data upon Condensers Used.

No.	End.	Length (cm.).	Extl. diam. of inner cyl. (cm.).	Int. diam. of outer cyl. (cm.).	Dielectrics used.
1	Whole.	20	5·9	6·1	Air; C_6H_6; CCl_4.
2	Half.	20	5·9	6·1	Air; C_6H_6.
3	Half.	5	5·9	6·1	,, ,,
7	Whole.	30	3·8	4·1	C_6H_6; $CHCl_3$.
8	Half.	30	3·8	4·1	,, ,,
9	Whole.	19	1·8	2·1	$CHCl_3$; $C_2H_4Cl_2$.
10	Half.	19	1·8	2·1	,, ,,
12	Whole.	14·8	1·8	2·3	$C_2H_4Cl_2$; o-$C_7H_7{\cdot}NO_2$.
13	Half.	14·8	1·8	2·3	,, ,,
14	Whole.	11·8	2·15	2·8	o-$C_7H_7{\cdot}NO_2$; $C_6H_5{\cdot}NO_2$.
15	Half.	11·8	2·15	2·8	,, ,,

TABLE II.

Dielectric Constant of Benzene.

(Normal "Half-end" Correction Method.)

Bridge: Schering and Semm's. Frequency: 1000 cycles per second.
Temperature: 25·00° ± <0·01°.

Condenser No.	Capacity. Air.	Capacity. Benzene.	Apparent D.C.	End corr.	D.C. of benzene. Corrected. Air = 1.	D.C. of benzene. True. Air = 1·0006 *
1	597	1322·5	2·2153	0·0308	2·2461	2·2474
,,	594·5	1317·5	2·2161	,,	2·2469	2·2482
,,	591	1310·2	2·2169	,,	2·2477	2·2490
		Mean	2·2161			
2	589·5	1316	2·2324	0·0154	2·2478	2·2491
,,	588·5	1312·5	2·2302	,,	2·2456	2·2469
,,	588·5	1313·5	2·2320	,,	2·2474	2·2487
		Mean	2·2315		Mean	2·2482
					Probable error	±0·0003

* This value is the mean of the following values: 1·00065 (Wagstaff), 1·00065 (Gill), 1·00060 (Carman and Lorance), 1·00054 (Fritts), 1·0005 (Boltzman), 1·0005 (Klemencie).

TABLE III.

Dielectric Constant of Benzene.

(Virtual Condenser Method.)

Condenser No.	Capacity. Air.	Capacity. Benzene.	Capacity of virtual condenser. Air.	Capacity of virtual condenser. Benzene.	D.C. of benzene (air = 1·0006).
3	101·5	220·5	487·25	1095·6	2·2498
,,	102·5	219·5	486·25	1092·1	2·2473
,,	102·75	221·25	486·25	1093·1	2·2493
Means	102·25	220·4		Mean	2·2488
				Probable error	± 0·0005

NOTE.—The capacities of the virtual condenser are obtained by subtraction of the mean capacities for condenser 3 from the appropriate capacities of condenser 2.

TABLE IV.

Dielectric Constant of Carbon Tetrachloride.

Bridge: Schering and Semm's. Frequency: 1000 cycles per second.
Temperature: 25·00° ± 0·01°.

Condenser No.	Capacity. Air.	Capacity. CCl_4.	Apparent D.C.
1	589·25	1290·1	2·1894
,,	590	1289·3	2·1853
		Mean	2·1873

Whence, assuming the relation of true to apparent D.C. to be the same (in the same condenser) for carbon tetrachloride as for benzene, the true dielectric constant of carbon tetrachloride = 2·1873 × 2·2482/2·2161 = 2·219 ± 0·002.

The arithmetical process adopted in the following tables needs some explanation. The condensers having been calibrated with a liquid of known dielectric constant, their capacities with other

liquids as dielectrics were observed. On repeating the calibration no change in the condenser was ever observed. Every capacity figure given in the tables is the mean of a series (at least four) of concordant observations. In calculating the apparent dielectric constant, the individual capacity figures of the condenser with the liquid of unknown dielectric constant as dielectric have been divided by the *mean* capacity figure of the condenser with the standard liquid as dielectric, and then multiplied by the known dielectric constant of the latter liquid. This method enables the "probable error" to be calculated in a satisfactory manner.

To obtain the results set out in the following tables, the parallel resistance method was employed, the frequency being 1000 cycles per second and the temperature of the dielectric 25·00° ± <0·01°.

TABLE V.

Dielectric Constant of Chloroform.

The parallel resistance was of the order of 325 × 10^8 ohms across a condenser of capacity 1096 $\mu\mu$f., whence the loss angle characteristic of the liquid is approximately 24°.

Condenser No. 7. Capacity.		Apparent	Condenser No. 8. Capacity.		Apparent
Benzene.	$CHCl_3$.	D.C.	Benzene.	$CHCl_3$.	D.C.
719	1472·25	4·6059	712·8	1465·75	4·6230
719	1471·5	4·6031	713·25	1463·25	4·6152
718·5	1466	4·5859	712·5	1464·5	4·6191
718·25	1465·5	4·5844	712·5	1464·25	4·6183
	1468·8	4·5946	712·95	1464·05	4·6178
	1469·7	4·5975		1462·75	4·6136
	1467	4·5890			
	1467·5	4·5906			
Means 718·7		4·5937	712·8		4·6178

The correction to be applied to these values is 0·0478 for condenser 7 and 0·0239 for condenser 8. The true dielectric constant of chloroform is therefore 4·6417 ± 0·001.

TABLE VI.

Dielectric Constant of Ethylene Dichloride.

Parallel resistance, about 232 × 10^3 ohms; capacity, 905 $\mu\mu$f.; whence the loss angle is approximately 35°.

Condenser No. 9. Capacity.		Apparent	Condenser No. 10. Capacity.		Apparent
$CHCl_3$.	$C_2H_4Cl_2$.	D.C.	$CHCl_3$.	$C_2H_4Cl_2$.	D.C.
646·75	1390	10·003	643	1396·3	10·068
645·45	1391	10·011	643	1396·65	10·071
644·05	1392·3	10·019	643	1397·75	10·079
644·3	1391·75	10·016	643·5	1396·5	10·072
645	1391·5	10·014	643·75		
644·5	1391	10·011	644		
644·5	1392·1	10·018	645		
645·5	1391·75	10·016	644·75		
Means 645·0		10·0135	643·75		10·0725

Correction: 0·118 for condenser 9 and 0·059 for condenser 10. Whence the true dielectric constant of ethylene dichloride is 10·131 ± 0·001.

TABLE VII.

Dielectric Constant of o-Nitrotoluene.

Condenser No. 12. Capacity.			Condenser No. 13. Capacity.		
$C_2H_4Cl_2$.	o-$C_7H_7{\cdot}NO_2$.	Apparent D.C.	$C_2H_4Cl_2$.	o-$C_7H_7{\cdot}NO_2$.	Apparent D.C.
581·5	1493·75	25·994	580·5	1489·5	25·988
582·25	1489·75	25·926	580·75	1490	25·997
582·45	1491·85	25·962	581	1490·35	26·003
582·5	1487·7	25·890	581	1488·25	25·967
582·5	1487·25	25·882	580·1	1492·1	26·034
582·15	1487·45	25·886	580·5	1492·25	26·036
	1487·1	25·880		1490·1	26·000
	1490·7	25·941		1488·05	25·964
	1487·9	25·893		1488·6	25·973
	1491·5	25·956			
	1492·75	25·977			
Means 582·16		25·926	580·64		25·996

Correction : 0·140 for condenser 12 and 0·070 for condenser 13. Whence the true dielectric constant of *o*-nitrotoluene is 26·066 ± 0·005.

TABLE VIII.

Dielectric Constant of Nitrobenzene.

Condenser No. 14. Capacity.			Condenser No. 15. Capacity.		
o-$C_7H_7{\cdot}NO_2$.	$C_6H_5{\cdot}NO_2$.	Apparent D.C.	o-$C_7H_7{\cdot}NO_2$.	$C_6H_5{\cdot}NO_2$.	Apparent D.C.
987·4	1289·8	34·101	976·1	1280	34·092
988·75	1284·6	33·956	979	1277·9	34·037
988·25	1289	34·072	978·25	1278·25	34·046
987	1286·6	34·008	978·25	1279·65	34·083
985	1285	33·966	979·6	1278·65	34·057
984·45	1286·75	34·012	980·6	1278	34·039
983·7	1286·85	34·016			
984·3	1286·8	34·014			
984·45					
985·25					
988					
986·8					
Means 986·1		34·018	978·63		34·059

Correction : 0·082 for condenser 14 and 0·041 for condenser 15. Whence the true dielectric constant of nitrobenzene is 34·093 ± 0·007.

Comparison of the Results.

In order to facilitate the comparison of the foregoing results with those of other investigations, the following tables, based chiefly on recent work, are given.

D.C.	Temp.	Observer.	Method and frequency.
		Benzene.	
2·288	18°	Turner.[1]	Bridge—telephonic.
2·27?	25	Grützmacher.[2]	Valve—radio.
2·27	17	Veley.[3]	Bridge—telephonic.
2·29	10	Errera.[4]	Bridge—radio.
2·268	25	Isnardi.[5]	Resonance—radio.
2·25	—	Klein.[6]	Resonance—radio.
2·268	25	Graffunder.[7]	Valve—radio.
2·24	16	Philip.[8]	Bridge—telephonic.
2·28	—	King and Patrick.[9]	Bridge—telephonic.
2·2402	25·5	Sayce and Briscoe.[15]	Resonance—radio.
2·2482	25	This work.	Bridge—telephonic.
		Carbon Tetrachloride.	
2·049	12·5°	Veley.[3]	Bridge—telephonic.
2·1831	25	Grützmacher.[2]	Valve—radio.
2·246	18	Turner.[1]	Bridge—telephonic.
2·314	25	Isnardi.[5]	Resonance—radio.
2·219	25	This work.	Bridge—telephonic.
		Chloroform.	
5·06	—	Joachim.[10]	Bridge—radio.
4·962	25°	Grützmacher.[2]	Valve—radio.
4·811	25	Tangl.[11]	Bridge—telephonic.
5·2	18	Turner.[1]	Bridge—telephonic.
4·760	25	Isnardi.[5]	Resonance—radio.
4·92	—	Klein.[6]	Resonance—radio.
4·93	18	Philip.[8]	Bridge—telephonic.
4·6417	25	This work.	Bridge—telephonic.
		Ethylene Dichloride.	
10·95	—	Joachim.[10]	Bridge—radio.
10·88	18°	Turner.[1]	Bridge—telephonic.
10·131	25	This work.	Bridge—telephonic.
		o-*Nitrotoluene.*	
26·58	15°	Thwing.[12]	Resonance—ultra radio.
27·71	18	Turner.[1]	Bridge—telephonic.
20·3	18	Mathews.[13]	Drude's—ultra radio.
26·066	25	This work.	Bridge—telephonic
		Nitrobenzene.	
32·19	15°	Thwing.[12]	Resonance—ultra radio.
36·41	18	Turner.[1]	Bridge—telephonic.
34·37	25	Jezewski.[14]	Resonance—radio.
35·57	10	Errera.[4]	Bridge—radio.
36·45	—	Joachim.[10]	Bridge—radio.
37·1	16	Philip.[8]	Bridge—telephonic.
34·093	25	This work.	Bridge—telephonic.

[1] *Z. physikal. Chem.*, 1900, **35**, 385. [2] *Z. Physik.*, 1924, **28**, 342. [3] *Phil. Mag.*, 1906, **11**, 73. [4] *J. Phys. Radium*, 1922, **3**, 401. [5] *Z. Physik.*, 1922, **9**, 153. [6] *Medd. K. Vetenskapsakad. Nobel Inst.*, 1918, **3**, No. 24. [7] *Ann. Phys.*, 1923, **70**, 225. [8] *Z. physikal. Chem.*, 1897, **24**, 18. [9] *J. Amer. Chem. Soc.*, 1921, **43**, 1835. [10] *Ann. Phys.*, 1919, **60**, 570. [11] *Ibid.*, 1903, **10**, 748. [12] *Z. physikal. Chem.*, 1894, **14**, 286. [13] *J. Physical Chem.*, 1905, **9**, 641. [14] *J. Phys. Radium*, 1922, **3**, 293. [15] This vol., p. 315.

Summary.

1. Alternating current bridge methods of determining the dielectric constants of liquids have been discussed critically and experimentally.

2. The method of Nernst and Turner has been criticised.

3. The dielectric constants of specially purified materials have been determined with an accuracy which the author claims has not been previously attained.

The author wishes to express his thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant which enabled him to undertake this work, and to Messrs. Brunner Mond and Co., whose assistance made possible the purchase of much of the apparatus employed in this investigation. Further, the author is deeply indebted to Prof. J. C. Philip, F.R.S., for much encouragement and help during the progress of the work.

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LONDON, S.W. 7. [*Received, February 26th*, 1925.]

CXLVIII.—*A Solid Antimony Hydride.*

By EDWARD JOSEPH WEEKS and JOHN GERALD FREDERICK DRUCE.

THE object of this research was the preparation of a solid antimony hydride,* Sb_2H_2, analogous to Janovsky's solid arsenic hydride (*Ber.*, 1874, **6**, 216; see also Weeks and Druce, *Chem. News*, 1924, **129**, 31, where references to other and more satisfactory methods for its preparation are given).

Sand, Weeks, and Worrell (J., 1923, **123**, 456) showed that the amounts of stibine formed at an antimony cathode during the electrolysis of solutions of sulphuric acid and of sodium hydroxide were definitely related to the temperature and concentration of the electrolyte. In calculating the yields of stibine from the alkaline electrolyte, however, smooth curves could be obtained only

* The names "arsenic dihydride" and "antimony dihydride" are suggested, in default of better, for the substances As_2H_2 and Sb_2H_2. The difficulty of nomenclature is increased by the fact that Moser and Brukl (*Monatsh.*, 1924, **45**, 25) state that they have obtained another solid arsenic hydride, As_4H_2, by passing arsine into a hydrochloric acid solution of stannic chloride:

$$5SnCl_4 + 4AsH_3 = As_4H_2 + 5SnCl_2 + 10HCl.$$

That statement has been confirmed, but whilst their product was amorphous, ours was distinctly crystalline.

Their method was not applicable to the preparation of solid antimony hydride.

by adding together the amount of stibine evolved (calculated from the amount of silver nitrate with which it interacted) and the amount corresponding to the "antimony" deposited in the sodium hydroxide solution. This amorphous deposit of "antimony" was therefore most probably formed by the action of the alkali upon the stibine. Since one of us (E. J. W.) had already observed that the solid deposited in the porous pot during the electrolysis of alkaline solutions at an arsenic cathode was arsenic dihydride, As_2H_2, the deposit of "antimony" was examined; it contained hydrogen and approximately 99% of antimony and proved to be antimony dihydride.

Reckleben and Scheiber prepared arsenic dihydride by the interaction (*Z. anorg. Chem.*, **1911, 70,** 255) of arsine with sodium hydroxide and decomposition of the resulting sodium arsenide with water. In consequence of this observation, which we have confirmed, and on the assumption that an atmosphere of hydrogen would favour the formation of antimony dihydride, mixtures of stibine with an excess of purified hydrogen were passed through solutions of sodium hydroxide of various strengths. Solutions stronger than 5*N* gave the desired compound, but the yields were always poor. The reactions which take place may be expressed thus:

$$SbH_3 + 3NaOH = Na_3Sb + 3H_2O.$$
$$2Na_3Sb + 6H_2O = 6NaOH + Sb_2H_2 + 2H_2.$$

Negative results were obtained when potassium hydroxide was used. Stibine was then passed over solid sodium hydroxide, which soon became coated with a grey deposit. This was decomposed with water, hydrogen being given off, and the residue, after treatment with dilute hydrochloric acid, washing, and drying over calcium chloride in a vacuum desiccator, was antimony dihydride.

The stibine used in these experiments was prepared by dropping a solution of antimony chloride in concentrated hydrochloric acid diluted with its own volume of water into a flask containing zinc and dilute hydrochloric acid. At the end of the experiment, the flask contained a quantity of grey residue, which was insoluble in dilute or concentrated hydrochloric acid. The hydrogen evolved from the zinc and acid, therefore, did not convert all (or even most) of the antimony into stibine; apparently the conditions favoured the formation of a lower hydride:

$$2SbCl_3 + 8H \longrightarrow Sb_2H_2 + 6HCl.$$

The compound contained a faint trace of iron,* but no zinc,

* This was also detected in the antimony chloride used; the zinc appeared to be free from iron.

carbon, or chlorine. It contained hydrogen, which it lost on heating in a vacuum, and which was converted into water when the substance was ignited in air or oxygen. A sample which had been kept over sulphuric acid in a vacuum desiccator for 14 days was heated in a vacuum, and the hydrogen evolved was measured and the residual antimony weighed: 0·6566 g. gave 29 c.c. of H_2, measured at N.T.P., and 0·6506 g. of Sb; H, 0·40; Sb, 99·14. 0·4720 g. gave 0·0357 g. of H_2O; H, 0·86. 0·4941 g. gave 0·6185 g. of Sb_2O_4; Sb, 98·85 (Sb_2H_2 requires Sb, 99·17; H, 0·83%).

Amorphous antimony dihydride dissolved in fairly strong nitric acid, but was insoluble in other dilute mineral acids and in concentrated hydrochloric or sulphuric acid. Concentrated nitric acid and dilute aqua regia (the most suitable dissolvent) readily attacked it. It was insoluble in solutions of the caustic alkalis.

When heated to dull redness in a current of hydrogen for ½ hour, the dihydride decomposed slightly, since a little elementary antimony was deposited on the cooler parts of the tube and a small amount of silver antimonide (indicating the formation of stibine) was produced when the escaping gas was passed through silver nitrate solution.

When the dihydride was heated sufficiently, it became incandescent, and then continued to glow until it was converted into a shining, brittle mass of elementary antimony. (Arsenic dihydride exhibits the same phenomenon, but not so strikingly.)

Since we have obtained antimony dihydride by the electrolysis of sodium hydroxide at an antimony cathode, our compound cannot be a variety of the well-known "explosive antimony" (Gore, *Phil. Mag.*, 1855, [iv], **9**, 73; J., 1863, **16**, 365; see also Cohen and Strengers, *Z. physikal. Chem.*, 1904, **50**, 291), which contains from 4·8 to 7·9% of antimony trichloride and, according to Pfeiffer (*Annalen*, 1881, **209**, 161), traces of hydrochloric acid.

Evidence that our product is neither an allotropic variety nor impure antimony was supplied by dilatometer experiments. Cohen and Bosch (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 645), in studying dilatometrically the allotropes of antimony, observed a transition point at 101°. When antimony dihydride was gradually heated with xylene in a dilatometer from 15° to 112°, no sharp change was observed at 101° or any other temperature.

The dihydride reacted vigorously with fused potassium nitrate, whilst with powdered (reduced) antimony no such action was observed, dissolution of the metal in the nitre taking place very slowly. The product left after heating the dihydride in a vacuum behaved like the reduced antimony in this respect.

The authors desire to thank the Research Fund Committee of the Chemical Society for a grant to one of them (J. G. F. D.) which has partly defrayed the expenses of this investigation.

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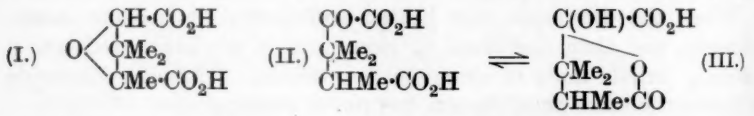
CXLIX.—*Ring-chain Tautomerism. Part XIV. The Structure of Balbiano's Acid.*

By EUGENE ROTHSTEIN, ARNOLD STEVENSON, and JOCELYN FIELD THORPE.

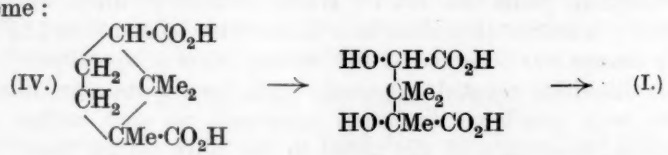
THE acid $C_8H_{12}O_5$, which Balbiano obtained from camphoric acid and to which he assigned the structure (I), has already been mentioned in Parts I and VII of this series (J., 1922, **121**, 650; 1923, **123**, 2852), and in the latter (Pandya and Thorpe) it was shown that the evidence led to a structure for this acid which represented it, in solution or in the liquid state, as an equilibrium mixture of the two tautomeric individuals (II) and (III), but that in all probability the solid substance melting at 120° was the hydroxy-ring form (III).



Nevertheless, there were many points which remained ambiguous, especially those in connexion with the arguments Balbiano brought forward in support of his formula, which have hitherto been regarded as conclusive.

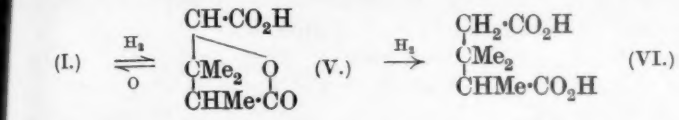
In order to make the position clear, it is necessary briefly to recount some of the more salient facts in the history of this acid, which is one that has played such an important part in the determination of the structure of camphor.

Balbiano prepared it by the slow oxidation of camphoric acid (IV) and, in the light of his final decision regarding its structure (I), considered that its formation took place in accordance with the scheme :



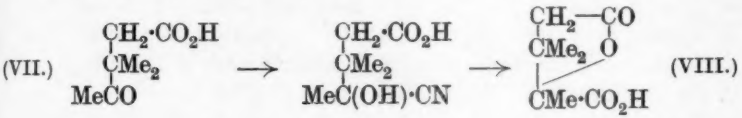
In the course of his experiments, Balbiano reduced the acid (I) to a lactonic acid, $C_8H_{12}O_4$, melting at 163°, to which he gave the

formula (V), and ultimately to αββ-trimethylglutaric acid (VI), the structure of which was proved by the synthesis of Perkin and one of us (J., 1899, **75**, 61). Balbiano was also able to oxidise



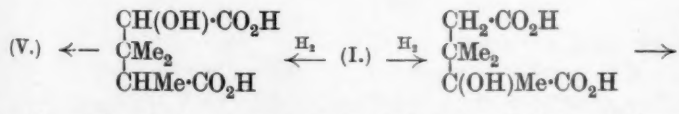
his lactonic acid (V) back to the original acid (I) by means of permanganate.

Blanc (*Bull. Soc. chim.*, 1901, **25**, 68), in his attempt to synthesise Balbiano's acid, prepared a lactonic acid melting at 163° isomeric with the lactonic acid (V), but which he found to be unaltered by permanganate. Blanc's lactonic acid was prepared from dimethyllævulic acid (VII) through the addition of hydrocyanic acid and hydrolysis and, therefore, could only have the structure (VIII). The discovery of this compound led Balbiano to re-examine the lactonic acid he had prepared by the reduction of his acid (I), with



the result that he was able to isolate, by means of the barium salts, two lactonic acids, one melting at 163° and the other at 165°.

The outcome is remarkable, because whilst Blanc states (*loc. cit.*) that Balbiano's lactonic acid depressed the melting point of his lactonic acid to about 115°, Balbiano asserts that this figure is incorrect (*Centr.*, 1902, II, 573), for in his hands the mixture of the lactonic acids prepared by him melted only 5° lower. Balbiano's conclusion is that by the reduction of his acid (I) he had prepared both the lactonic acids (V) and (VIII) and it is this proof which he, quite rightly, regarded as decisive, since it is only possible to obtain these substances from his "oxide" formula, and any other expressions, such as, for example, the ketone formula of Mahla and Tiemann become untenable.



Here the matter rested until 1923, when Pandya and one of us (*loc. cit.*) isolated both Blanc's lactonic acid (m. p. 165·5°) and Balbiano's lactonic acid (m. p. 163°) from the products obtained by the monobromination of αββ-trimethylglutaric acid, and it was then

that the first doubts as to the correctness of Balbiano's observations arose, because Blanc's statement that the mixture of the two substances melted at about 115° was confirmed (*loc. cit.*, p. 2863). It was clear, therefore, that Balbiano could not have used Blanc's lactonic acid in the experiment he describes.

The two lactonic acids prepared by Pandya and Thorpe were obtained in very different proportions, the higher-melting compound largely predominating. It was clear that they were derived from the only two monobromo-derivatives possible, namely, (IX) and (X),

but there was no evidence to show which was which. The higher-melting compound was, however, clearly identical with that prepared by Balbiano by a very similar method and to which he assigned the structure (V), although he did so merely on the ground that bromination of αββ-trimethylglutaric anhydride would *probably* lead to the bromo-acid (X). In the same paper, he stated that the compound was also obtained by the reduction of the acid, m. p. 120°, although he does not mention having made a direct comparison of the two products (*Rend. Accad. Lincei*, 1899, **8**, 422).

A review of the whole subject showed the existence of many ambiguities and contradictions, which could only be removed in a satisfactory manner by preparing Blanc's lactonic acid (VIII) and carrying out a series of direct comparisons. At the time this difficult preparation could not be accomplished, but it has now been carried out and the chemistry of this important chapter in the history of the structure of camphor is, at last, quite clear. The position may be summarised as follows:

(1) The lactonic acids prepared by Balbiano by the reduction of the acid, m. p. 120°, are not identical with Blanc's synthetic lactonic acid. We have carefully repeated the reduction and have isolated a lactonic acid, m. p. 162—163°, which depressed the melting point of the synthetic acid some 40° in accordance with Blanc's observation. The lactonic acid, m. p. 162—163°, was the sole product of the reaction; we have made repeated attempts to resolve it into two components as described by Balbiano (*loc. cit.*), but without success. It may be mentioned that an acid of the formula (V) can exist in two stereoisomeric modifications, of which the compound, m. p. 162—163°, prepared by Balbiano and by ourselves must be one. Balbiano's observation that the alleged mixture of the two compounds (in the ratio 2 : 1) originally obtained melts at 163°, whilst a mixture of equal parts of his two pure isomerides melts

at 158° is clearly unsatisfactory, but it proves quite definitely that the second substance, if any, present in the original mixture cannot have been Blanc's lactonic acid. Mixtures of this acid with the acid, m. p. 162—163°, in widely different proportions melt very much lower, as already mentioned.

(2) Blanc's lactonic acid has the formula (VIII) and can exist only in one inactive modification. As already stated, it is not produced by the reduction of Balbiano's acid, but is, however, the chief product formed in the monobromination of αββ-trimethylglutaric acid.

As regards the melting point of Blanc's lactonic acid, it is clear that the figure given by Blanc is too low and should have been 165·5°.

(3) The lactonic acid melting at 165·5—166° described by Pandya and Thorpe has the formula (VIII) and not the formula (V), and that melting at 163° has the formula (V) and not the formula (VIII). The descriptions of these substances must therefore be interchanged in the reference cited. It is unfortunate, but was in the circumstances inevitable, that the lactonic acid melting at 163° should have been used for the purpose of identifying the lactonic acid prepared by Chandrasena, Ingold, and Thorpe (J., 1922, **121**, 1550) from α-campholytic acid on oxidation, and that the identity of the two should have been advanced by them as proof of the existence of a bridged phase in α-campholytic acid. It is now clear that the lactonic acid prepared by these investigators has the formula (VIII) and that the supposed " proof " is without significance.

It follows, therefore, that Balbiano's " oxide " formula for the acid $C_8H_{12}O_5$ is incorrect and that the evidence brought forward in Parts I and VII of this series, which need not be recapitulated here, shows conclusively that this substance exhibits keto-cyclol tautomerism of the kind suggested. In order, however, still further to confirm this and, incidentally, to ascertain if other compounds, similar in structure to the lactonic acid (V), also exist in stereoisomeric forms which also possess similar melting points and show no mutual depression of the melting point when mixed, we have carried out a series of comparative experiments between Balbiano's acid (I) and the next lower homologue.

It is a curious fact that this substance was prepared, and its properties studied, many years ago by Perkin and one of us (J., 1901, **79**, 729) and was isolated only in the hydrated form (XI), but we now find that it can readily be converted into the diethyl ester and that this does not contain water of hydration. It must therefore have the structure (XII). Balbiano's acid also can be easily converted into the diethyl ester and since, in this compound,

there is no possibility of the occurrence of tautomerism, it must have the structure (XIII). The two esters, therefore, are directly

(XI.) $C(OH)_2 \cdot CO_2H$ / CMe_2 / $CH_2 \cdot CO_2H$ (XII.) $CO \cdot CO_2Et$ / CMe_2 / $CH_2 \cdot CO_2Et$ $CO \cdot CO_2Et$ / CMe_2 / $CHMe \cdot CO_2Et$ (XIII.)

comparable and should, if our hypothesis is correct, serve as bases for the comparative experiments we have outlined.

It will be noticed that if the keto-ester (XII) is treated with ethyl bromoacetate and zinc (the usual Reformatski reaction), it should be converted into a hydroxy-tribasic ester (XIV) which should lose ethyl alcohol on distillation and yield the lactone of a dibasic ester (XV), which can exist in only one inactive modification.

(XIV.) $CO_2Et \cdot CH_2 \cdot C(OH) \cdot CO_2Et$ / CMe_2 / $CH_2 \cdot CO_2Et$ $CO_2Et \cdot CH_2 \cdot C \cdot CO_2Et$ / CMe_2 — O / CH_2 — CO (XV.)

(One inactive form.)

On the other hand, if the ester (XIII) were treated in a similar manner, the lactonic dibasic ester (XVII) which will be formed from the hydroxy-tribasic ester (XVI) on distillation will be capable of existence in two inactive modifications. Experiment shows this

(XVI.) $CO_2Et \cdot CH_2 \cdot C(OH) \cdot CO_2Et$ / CMe_2 / $CHMe \cdot CO_2Et$ $CO_2Et \cdot CH_2 \cdot C \cdot CO_2Et$ / CMe_2 — O / $CHMe \cdot CO$ (XVII.)

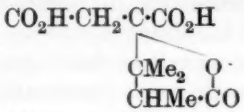
(Two inactive forms.)

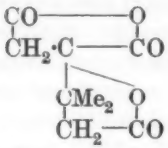
to be the case. The lactonic dibasic ester (XV) is obtained in one well-defined form, and the lactonic ester (XVII) in two distinct stereoisomeric modifications, m. p. 86° and 115°, respectively. These two substances cause a considerable depression in the melting point when mixed, and this observation further strengthens our belief that Balbiano could not have isolated the two stereoisomerides of the lactonic acid (V) predicted by theory.

On hydrolysis, both the stereoisomeric esters give the same lactonic acid, m. p. 178° (XVIII), whilst a second isomeric acid, m. p. 140°, is isolated from the higher-melting ester. The acids, m. p.'s 178° and 140°, are doubtless stereoisomerides like the ester, the lower-melting lactone probably having the *cis*-structure, as it decomposes at the melting point; the product is probably an anhydride analogous to (XIX) described below.

The ester (XV) can be hydrolysed in the same way to the corresponding lactonic acid, which passes very readily to the anhydride

(XIX); in fact the change takes place on keeping the acid, so that the two are generally obtained together.

(XVIII.) 

 (XIX.)

It is perhaps interesting to note, especially in view of the different opinions which are held regarding the intervention or non-intervention of water in the mutarotation of sugars, that when the molecular conditions are present, as is the case in Balbiano's acid, which lead to tautomeric change in solution or in the liquid state, the substance shows no tendency to exist in the hydrated form. If, however, as in the next lower homologue, these conditions are absent, the ketone exists in the hydrated state and only passes into the anhydrous condition when the water is driven off by heat. The fact, therefore, that the mutarotatory sugars are not hydrated is significant.

Experimental.

α-Keto-ββ-dimethylpentane-αγ-dicarboxylic Acid (*Balbiano's Acid*).—Balbiano's directions for preparing the acid (*Rend. Accad. Lincei*, 1892, **1**, 278; *Ber.*, 1894, **27**, 2133) were followed, but, as at the ordinary temperature decoloration of the permanganate took some months, the oxidation was carried out at 28—30°, when it was completed in from 4 to 6 weeks. The yield from 450 g. of camphoric acid was about 80 g. of the calcium salt, from which about 45 g. of the acid were obtained. Previous investigators were unable to recrystallise the acid, but from a very concentrated solution in chloroform it separates in stellate clusters of prisms [Found: C, 51·0; H, 6·4; *M* (dibasic), 92. Calc., C, 51·0; H, 6·4%; *M*, 94].

The *diethyl* ester (XIII), a slightly viscous liquid, b. p. 148—149°/11·5 mm., is best prepared by Phelp and Tillotson's alcohol vapour method (yield 75%), as the ordinary methods give very poor results (Found: C, 58·4; H, 8·25. $C_{12}H_{22}O_5$ requires C, 59·0; H, 8·3%).

γ-Lactone of α′-Hydroxy-αββ-trimethylglutaric Acid (V).—A mixture of Balbiano's acid (12 g.), hydriodic acid (*d* 1·7; 40 c.c.), and red phosphorus (4 g.) was heated under reflux for 5 hours, diluted with water, the excess phosphorus filtered off, and the filtrate extracted with ether. The ethereal extract was successively washed with water, sodium thiosulphate, and again with water, and the ether removed. The residue was dissolved in water, neutralised with sodium hydroxide, and boiled with calcium chloride (30%), when calcium trimethylglutarate was precipitated (Balbiano, *loc. cit.*).

The filtrate was acidified with hydrochloric acid and extracted with ether; the extract on evaporation gave a solid which on crystallisation from ethyl acetate and light petroleum (b. p. 40—60°) melted at 163° (Found: C, 55·6; H, 7·1. Calc., C, 55·8; H, 7·0%). Repeating Balbiano's work, the barium salt of this lactonic acid was fractionally crystallised and the acids were regenerated from the two fractions, but it was found that the melting points were 162—163° and 163—164°, respectively, and that there was no depression of the m. p. when the two were mixed.

γ-Lactone of α-Hydroxy-αββ-trimethylglutaric Acid (*Blanc's Lactone*) (VIII).—ββ-Dimethylsuccinic acid, prepared from acetone cyanohydrin and ethyl cyanoacetate (Higson and Thorpe, J., 1906, **89**, 1465), was heated under reflux with acetyl chloride to form the anhydride (b. p. 110°/16 mm.), and from this the chloride of α-carbethoxy-β-methylpropane-β-carboxylic acid, $CO_2Et{\cdot}CH_2{\cdot}CMe_2{\cdot}COCl$, was obtained as described by Blaise (*Compt. rend.*, 1899, **128**, 183). Instead of converting this into ethyl ββ-dimethyl-lævulate with zinc methyl, it was found more convenient to employ the Blaise-Maire method (compare Birch, Kon, and Norris, J., 1923, **123**, 1370) (yield 78%). The acid obtained by the hydrolysis of this ester was treated with potassium cyanide, and the resulting nitrile hydrolysed as described by Blanc (*loc. cit.*); the lactonic acid separated from water in needles, m. p. 165·5° (Found: C, 55·9; H, 7·25. Calc., C, 55·8; H, 7·0%). The m. p. of the mixture with the γ-lactone of α′-hydroxy-αββ-trimethylglutaric acid was 116—117°.

γ-Lactone of δε-Dicarbethoxy-δ-hydroxy-γγ-dimethylpentane-β-carboxylic Acid (XVII).—A mixture of ethyl α-keto-ββ-dimethylpentane-αγ-dicarboxylate (24·4 g.), ethyl bromoacetate (11·1 c.c.), benzene (50 c.c.), and zinc wire (6·5 g.) was heated under reflux on the steam-bath. Reaction only took place when a crystal of iodine was added and required 3—4 hours for completion. It can be accelerated by adding a small quantity of magnesium filings, but the yield is considerably reduced thereby. The product was isolated in the usual manner and distilled, when the main portion, b. p. 180—220°/20 mm. (yield 6—7 g.), solidified on cooling. The solid was crystallised from light petroleum (b. p. 40—60°), to which a few drops of benzene were added, and gave two distinct types of crystals which were separated by hand. On recrystallisation from the same solvent, these gave, respectively, needles, m. p. 86° (Found: C, 58·6; H, 7·8. $C_{14}H_{22}O_9$ requires C, 58·7; H, 7·8%), and minute prisms, m. p. 115° (Found: C, 58·7; H, 7·9). The m. p. of the mixture was 75°. It was subsequently found that a better separation was obtained by dissolving the crude substance in dilute alcohol, from which the lactone, m. p. 115°, separates more readily.

Products of hydrolysis. The lactone, m. p. 115° (2·5 g.) was heated under reflux for 5 hours with 50% aqueous potassium hydroxide (50 c.c.). The resulting solution was acidified and extracted with ether, the ethereal extract yielding a solid, which effervesced on treatment with sodium hydrogen carbonate and, after crystallisation from ethyl acetate and light petroleum (b. p. 40—60°), melted at 140° *with* decomposition (Found: C, 51·5; H, 6·2. $C_{10}H_{14}O_6$ requires C, 52·2; H, 6·1%). On keeping the mother-liquor, a second acid separated melting at 178° *without* decomposition (Found: C, 52·7; H, 6·3%). A mixture of the two acids melted at 122—125°.

The lactone, m. p. 86°, on similar treatment yielded a product which on crystallisation from ethyl acetate and light petroleum (b. p. 40—60°) melted at 122—125° and was probably a mixture of the two acids described above. None of the acid, m. p. 140°, could be isolated, as repeated crystallisation only gave acid, m. p. 178°, which was identical with that described above. If the esters are hydrolysed with hydrochloric acid (10%) instead of with potassium hydroxide, only 1 mol. of alcohol is eliminated. The lactone, m. p. 86°, gives an acid which after crystallisation from benzene and light petroleum has m. p. 146° (Found: C, 55·9; H, 7·25. $C_{12}H_{18}O_6$ requires C, 55·8; H, 7·0%); that from the lactone, m. p. 115°, crystallised from the same solvent, has m. p. 123° (decomp.) (Found: C, 56·4; H, 7·2%). When mixed, the two acids melted at 113°.

Ethyl α-keto-ββ-diethylglutarate * (XII) was obtained by a modification of Singh and Thorpe's method (J., 1923, **123**, 120) for the preparation of the corresponding methyl-ethyl acid.

Ethyl Methoxycaronate, $Me_2C<\begin{matrix}C(OMe)\cdot CO_2Et\\ CH\cdot CO_2Et\end{matrix}$.—Ethyl αα′-dibromo-ββ-dimethylglutarate (150 g.) was slowly added to 20 g. of sodium in 300 c.c. of methyl alcohol, and the mixture heated under reflux for 5 hours. The excess of alcohol was evaporated and the residue dissolved in water, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal extract, after washing with dilute sodium carbonate, gave an oil, b. p. 120°/18 mm. (Found: C, 58·5; H, 7·5. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·1%).

α-Keto-ββ-dimethylglutaric Acid.—Ethyl methoxycaronate (70 g.) (or the acid) and hydrobromic acid (*d* 1·5; 500 c.c.) were gently heated on a sand-bath, special caution being observed in the case of the ester, and finally boiled for 2 hours. On evaporation, a dark coloured solid remained, which was the acid in its hydrated form, m. p. 84° (yield nearly theoretical).

The acid was esterified with alcohol and sulphuric acid, the ester

* For this and the following experiments, we are indebted to Dr. B. Singh.

boiling at 140—141°/13 mm. (Found : C, 58·0; H, 8·1. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·8%).

Lactone of γδ-Dicarbethoxy-γ-hydroxy-ββ-dimethylbutane-α-carboxylic Acid (XV).—The keto-ester was treated with ethyl bromoacetate and zinc as described above, the operation requiring 7—8 hours for completion. The product on distillation yielded a thick oil, b. p. 198—204°/9 mm. (Found : C, 56·8; H, 7·6. $C_{13}H_{20}O_6$ requires C, 57·3; H, 7·3%), which on keeping formed a crystalline mass, m. p. 54°.

Products of hydrolysis. The ester (36 g.) was boiled for 3 hours with sodium hydroxide (36 g.) in 145 c.c. of water and 230 c.c. of alcohol, the alcohol being then evaporated off. Water was added and the acidified liquid extracted with ether, the ethereal extract yielding on evaporation a mixture of two substances which were readily separated by treatment with ether. The insoluble portion is the acid corresponding to the lactone, m. p. 54°. It melts at 132° (decomp.) [Found : C, 49·9; H, 5·5. $C_9H_{12}O_6$ requires C, 50·0; H, 5·6%. Silver salt : Found, Ag, 58·1. Calc. (tribasic), Ag, 58·3%]. The soluble portion is evidently the anhydride of the above acid (XIX). Crystallised from benzene, it formed shining needles, m. p. 126—128° (Found : C, 54·3; H, 5·0. $C_9H_{10}O_5$ requires C, 54·5; H, 5·0%). It is also formed when the acid is kept for some days.

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CL.—*Studies of Dynamic Isomerism. Part XVII. The Mutarotation of Aluminium Benzoylcamphor.*

By IRVINE JOHN FAULKNER and THOMAS MARTIN LOWRY.

THE preceding paper of this series (J., 1924, **125**, 2081) described the discovery in beryllium benzoylcamphor * of a new type of mutarotation, which differs fundamentally from the familiar mutarotation of prototropic compounds in that (i) it occurs in a compound containing no mobile hydrogen atom, and (ii) instead

* The formula from which the theoretical composition of this compound was calculated was given erroneously as $C_{34}H_{38}O_2Be$ instead of $C_{34}H_{38}O_4Be$ on pp. 2087 and 2088 of this paper.

of being arrested, it is accelerated in a remarkable degree in solutions in chloroform, with which the solute also forms a crystalline addition compound. The mutarotation was therefore attributed to a reversal of sign in an optically active beryllium atom, forming the centre of a fourfold co-ordination complex, in which both chelate groups are themselves optically active. The optical activity of a coloured metal in a complex of this kind can sometimes be detected by means of the Cotton phenomenon, which has been observed in the case of *copper*, *tervalent cobalt*, and *chromium*, but not in bivalent *nickel* and *cobalt* (Lifschitz, *Z. physikal. Chem.*, 1923, **105**, 27), where the four co-ordination positions may have a square instead of a tetrahedral configuration. In the case of *aluminium*, the absence of visible colour makes this method of detecting the optical activity of the metal impracticable, but enables us to look for it by observations of mutarotation.

Aluminium benzoylcamphor has now been observed to undergo mutarotation in four different solvents. The observed changes represent only a small fraction of the rotatory power of the compound, but they are quite unmistakable, since the total change of about 3° in the actual readings for a solution in benzene corresponds with an alteration of 30° in the specific rotatory power, and of about 200° in the molecular rotatory power of the compound. Mutarotation has also been observed in solutions in ethylene bromide, chloroform, and acetone. The mutarotation in ethylene bromide was very slow, extending over a period of about a week. In acetone and in chloroform, just as in the case of the beryllium compound, the change was rapid, the action being complete in the course of a few minutes, instead of extending over several days. The fact that the mutarotation in chloroform is in the opposite direction to that in benzene, ethylene bromide, or acetone, was confirmed by repeating the observations. It suggests, even if it does not prove, the formation in solution of a chloroform compound of higher rotatory power than the original material. The reversibility of the chemical changes by which the mutarotation is brought about was proved, as in the case of the beryllium compound, by recovering the original material and repeating the mutarotation both in benzene and in chloroform.

The curves showing the mutarotation of beryllium benzoylcamphor in benzene showed a well-marked lag, followed by a progressive speeding up of the action, but nothing of the kind was observed in solutions to which pyridine was added. The lag was therefore obviously due to the fact that *the mutarotation in benzene is not spontaneous*, but depends (like that of nitrocamphor and the sugars) on the intervention of a catalyst, which is gradually picked

up by the solution, *e.g.*, from the vessel in which it is examined. The curves for solutions containing pyridine were, moreover, at least approximately monomolecular in form; and although the velocity coefficients show the usual slight fluctuations, they are sufficiently exact to prove that *the mutarotation of beryllium benzoylcamphor obeys the monomolecular law.* This is no longer true for the solutions now under discussion, since *the velocity of mutarotation of aluminium benzoylcamphor falls off much more rapidly than a monomolecular law would allow.* The data indeed suggest that the mutarotation in benzene is probably governed by a trimolecular law, since the velocity of change is approximately proportional to the *cube* of the concentration, although the trimolecular velocity coefficients vary appreciably during the course of the change. This result may perhaps be associated with the necessity for inverting the points of attachment of *three* chelate groups in order to reverse the optical activity of the aluminium.

Experimental.

Aluminium benzoylcamphor was prepared by the method used by Burgess and Lowry for the preparation of beryllium benzoylcamphor (J., 1924, **125**, 2087). A slight excess of "pure" aluminium sulphate, dissolved in hot water, was added to equivalent quantities of piperidine and of benzoylcamphor dissolved in hot alcohol. The brownish-red precipitate, collected after heating on the water-bath for ½ hour, was washed with hot alcohol and crystallised from chloroform–acetone, a small yield of colourless material being obtained after a large number of recrystallisations. By observing the absorption spectrum, the colour was proved to be due to traces of iron from the aluminium sulphate; by adding successive small portions of benzoylcamphor (with its equivalent of piperidine) to the whole of the aluminium sulphate, however, most of the iron was removed in the first two fractions and the final fraction was almost colourless.

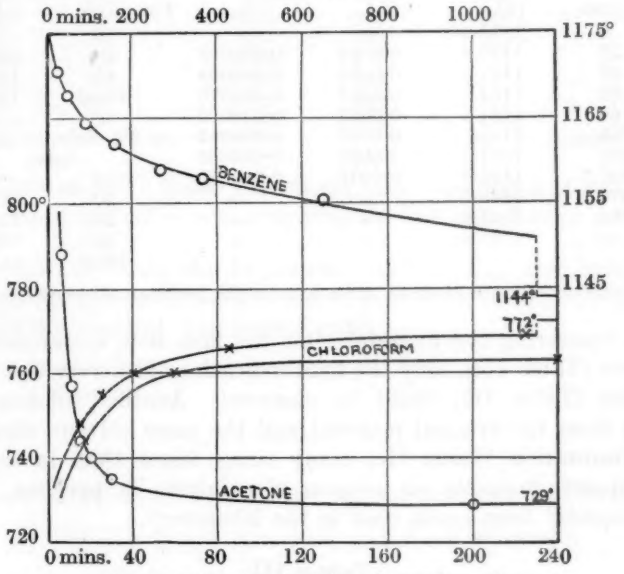
The compound forms microscopic crystals, and all attempts to grow crystals for measurement were unsuccessful; under the microscope these crystals appear as plates, which resemble the chromium compound. After two crystallisations the compound melted at 227—228° (Found: C, 76·8; H, 7·4; Al, 3·5. $C_{51}H_{57}O_6Al$ requires C, 77·2; H, 7·25; Al, 3·4%).

Aluminium benzoylcamphor is insoluble in aqueous solvents, and only slightly soluble in acetone and ethyl acetate; it is deposited as a glass from cold benzene (which dissolves about 5%) and from chloroform (which dissolves about 30%), but can be prepared in a crystalline form by adding two volumes of acetone

to a saturated solution in chloroform or benzene. Crystallisation is complete only after several weeks.

Mutarotation.—On account of its colour and limited solubility, the substance (which had been crystallised from chloroform–acetone and dried in a vacuum for 7 days) was examined in a 2½% solution in chloroform or benzene, and in a saturated solution in acetone or ethylene bromide.

FIG. 1.



Mutarotation of aluminium benzoylcamphor.

TABLE I.

Mutarotation in Chloroform.

2½% Soln. in 4-dcm. tube at 20°.			2½% Soln. in 2-dcm. tube at 20°.		
(*a*) Time (min.).	$[\alpha]_{5461}$.	k_{mono}.	(*b*) Time (min.).	$[\alpha]_{5461}$.	k_{mono}.
0	(730°)	—	0	(718°)	—
15	748	0·037	17	744	0·051
25	755	0·036	60	760	—
40	760	0·031	Final	763	
85	766	0·023			
235	769	0·014			
Final	772				

After the mutarotation recorded in Table I*a* was complete, 20 c.c. of the solution were evaporated twice to dryness with chloroform and acetone to give a crystalline product, made up again to 20 c.c. with chloroform, and re-examined in a 2-dcm. tube,

when the data of Table I*b* were recorded. The "velocity coefficients" (for a monomolecular action) were of the same order of magnitude as before, but the second mutarotation was distinctly faster than the first, probably because the material was less pure.

TABLE II.

Mutarotation in Benzene at 20°.

(*a*) 2½% Soln. in 4-dcm. tube.				(*b*) 2½% Soln. in 2-dcm. tube (recovered from II*a*).	
Time (min.).	$[\alpha]_{5461}$.	$k_{mono.}$	$k_{tri.}$	Time (min.).	$[\alpha]_{5461}$.
0	(1175·0°)	—	—	0	—
25	1170·5	0·0062	0·000055	30	1156·6°
48	1167·7	0·0055	0·000068	45	1155·6
90 *	1164·3	0·0047	0·000070	Final	1155·2
160	1161·8	0·0034	0·000062		
265	1158·9	0·0027	0·000062	(*c*) 2% Soln. in 4-dcm. tube.	
365	1157·8	0·0022	0·000055		
650 *	1155·3	0·0016	0·000050	0	—
1470 *	1149·5	—	—	20	1175·0
1890	1147·6	—	—	25	1161·5
Final	1143·8	—	—	32	1154·9
				Final	1154·1

* Water-circulation stopped during the night between these two readings.

On recovering the material after the first slow mutarotation in benzene (Table II*a*), only the final indications of a very fast mutarotation (Table II*b*) could be observed. Another solution, prepared from the original material and the same solvent, also gave a mutarotation (Table II*c*) many times faster than in the first experiment, probably on account of catalysis by pyridine, which had recently been much used in the laboratory.

TABLE III.

Mutarotation in Acetone at 20°.

Time (min.)	0	6	11	15	20	30	Final (24 hrs.)
α_{5461}	—	6·75°	6·48°	6·37°	6·34°	6·29°	6·24°
$[\alpha]_{5461}$	—	788	757	744	740	735	729

The solution was prepared by shaking the finely-divided solid with acetone for 5 minutes and then filtering into the tube. The concentration was estimated by evaporating 10 c.c. to dryness and weighing the residue.

The solutions were prepared by shaking 0·4 g. of the salt with about 30 c.c. of solvent and filtering; the concentration of the second solution was determined by evaporation, and that of the first solution was calculated to give the same final specific rotatory power.

In Table IV*a* the water-circulation was maintained during the first 6 hours but not during the subsequent nights; but all readings

TABLE IV.

Mutarotation in Ethylene Bromide.

Saturated soln. in 4-dcm. tube.

(*a*) $[a] = 22{\cdot}0$ *a*.		(*b*) $[a] = 22{\cdot}5$ *a*.			
Time (min.).	$[a]_{5461}$.	Time (min.).	$[a]_{5461}$ obs.	$[a]_{5461}$ calc.	Obs.—calc.
		20	583°		
30	570°	23	576		
45	566	25	574		
75	565	30	569	570°	−1°
195	564	45	567	568	−1
360	562	100	564	564	±
1320	558	300	561	556	+5
1860	553	530	557	552	+5
2820	550	1560	547	547	±
4200	546	2100	545	545	±
5640	545	2880	542	544	−2
9 days (final)	538	Final	538	538	±
				Mean $k = 0{\cdot}0000040$	

were taken at 20°. Table IV*b* shows that after the first half-hour the course of the curve conforms roughly to a *trimolecular* law.

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CLI.—"*Activated*" *Graphite as a Sorbent of Oxygen.*

By DONALD HUGH BANGHAM and JOHN STAFFORD.

IN the course of an investigation of the disappearance of hydrogen in discharge tubes, it was noticed that the graphite cathode, which had been made to take up relatively large quantities of hydrogen under the influence of the discharge, showed remarkably enhanced activity as a sorbent of ordinary (*i.e.*, molecular) oxygen. This circumstance was not in itself surprising in view of the experiments of Langmuir on atomic hydrogen, in which it was shown that the glass surfaces which had been exposed to hydrogen at low pressures in the presence of hot metallic filaments were capable of taking up measurable quantities of oxygen when the filaments had been allowed to cool and the hydrogen replaced by the latter gas (Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 1310). Nevertheless, it seemed worth while to examine in some detail the kinetics of the oxygen disappearance, in order to see whether, and how far, the time-equations governing it would differ from those previously found to hold for cases of sorption of a more usual type.

Investigation showed that the sorption of oxygen, both by the original and by the hydrogen-treated graphite, took place at constant pressure in obedience to an equation of the type

$$s = kt^b,$$

s being the quantity of oxygen sorbed at time t after its introduction to the graphite, and k and b being constants. The sorption is therefore exactly similar in type to that of ammonia, carbon dioxide, nitrous oxide, etc., on glass, the same anomalous time-law holding in these instances (Bangham and Burt, *Proc. Roy. Soc.*, 1924, *A*, **105**, 481).

Experimental.

The graphite used was a sample of the artificial variety supplied by the Acheson Graphite Co. A small glass bulb carrying a short platinum electrode at the bottom was partly filled with the finely-powdered material and sealed at its open end to a stem of quill tubing provided with a second electrode at some 10 cm. from the junction. The open end of the quill was sealed to a wide-bore tap which communicated with a gas-measuring system comprising a McLeod gauge and a calibrated tube containing phosphorus pentoxide. Other taps connected the measuring system through pentoxide tubes with the hydrogen and oxygen trains, and with the pumps. A rapid-acting type of high-vacuum pump was used, backed by a double-fall Sprengel which exhausted the gas to the water-pump. This pumping system was capable of maintaining over the heated graphite, even when it was parting with gas at a detectable rate, a pressure quite unmeasurable by the McLeod gauge.

After the graphite had been thoroughly exhausted in the cold, its temperature was raised to 350° and the pumping continued. Although graphite is usually considered inactive as a sorbent, this treatment caused it to yield considerable quantities of gas, and the rate of evolution became inappreciable only after several hours. The vacuum-heating was normally continued for about 72 hours, but no claim can be made that the graphite was rendered gas-free by this treatment, and there is no doubt that a rise of temperature above 350° would have led to further evolution. The treatment was nevertheless sufficient to secure that on allowing the solid to stand for 24 hours at room temperature no detectable gas developed in the system, whilst even at 350° the further evolution during the same period amounted to only a few cubic millimetres (N.T.P.).

The Disappearance of Hydrogen under the Influence of the Discharge.

The graphite, even after vacuum-heating, showed no tendency to take up measurable quantities of molecular hydrogen. This

fact, which was established by making a water-calibration of the containing bulb, enabled the deadspace volumes of bulbs subsequently used to be determined with hydrogen.

Immediately the discharge was begun the disappearance of the hydrogen was rapid, and it slowed down only when the pressure of the gas had fallen considerably. The particles near the surface of the graphitic cathode were thrown into a state of turbulence, and flashes of white light appeared in the same region. As the discharge continued, the graphite formed a coating on the surface of the tube which crept gradually upwards towards the anode, but fell back in patches and left the glass clear. At low pressures, the creeping of the graphite was more marked, the graphite gradually coating the tube from cathode to anode. Attempts to prevent this creeping by inserting a plug of glass wool in the stem of the tube led invariably to the fracturing of the tube at this point. In the absence of the plug, the tube frequently fractured opposite the upper surface of the graphite, practically all the heat being developed in this region.

If at any time the discharge were cut off, the pressure remained perfectly constant until its renewal.

Undoubtedly a certain amount of electrolysis of the glass took place, and the glass walls may also have contributed to a minute extent to the disappearance of hydrogen. A blank experiment, in which no graphite was used, showed, however, that the pressure changes caused by action at the surfaces of the glass and of the platinum wires amounted only to about 0·2% of those normally experienced.

The General Nature of the Phenomenon.

The following description of a series of typical experiments will serve to illustrate the general nature of the phenomenon. The amount of graphite used was 11 g. In order to render as comparable as possible the tests of its activity towards oxygen and carbon dioxide the gases were invariably introduced at the same pressure (*ca.* 0·4 mm.). In cases where the activity of the graphite was small, this pressure remained almost constant throughout the experiment; in other cases, it was necessary on occasions to renew the supply of gas in the system to approximate to this condition.

I. After the graphite had been submitted to vacuum-heating for the normal period of 72 hours, its "original" activity towards oxygen was determined. The sorption values at different times are given in Table I (Column A), in juxtaposition to those calculated from the equation $s = 2{\cdot}9 \times t^{0{\cdot}190}$.

II. The oxygen was pumped out, and the graphite submitted to

a further 18 hours' vacuum-heating, following which its activity towards oxygen was redetermined. The results appear in column B of the table together with those calculated from the equation $s = 2{\cdot}7 \,.\, t^{0{\cdot}190}$. The original activity of the graphite was therefore in the main reproducible simply by heating and pumping off the gas.

III. The graphite, after a further 18 hours' vacuum-heating, was submitted (as cathode) to the electric discharge in hydrogen by connecting the platinum wires to the terminals of a powerful coil. The gas was rapidly taken up, some 3 to 4 c.c. disappearing in the course of 2 hours. The dead-space hydrogen was then pumped out in the cold (the absorbed gas showed no tendency to leave the graphite), and a third oxygen-sorption experiment was performed. The earlier results were again in agreement with the above form of equation, but the value of k required was about 12 times greater than previously. The deviations from the formula were small, even in the later stages, *in spite of the fact that the pressure had fallen almost to one-third of its initial value.* After the pressure had been again raised to near its original value, the deviations ultimately tended towards zero. The recorded sorption-values are given in Column C of Table I, together with the s-values calculated from the equation $s = 34 \,.\, t^{0{\cdot}190}$.

The disappearance of the oxygen therefore showed all the characteristics of ordinary gas-sorption, its rate depending only to a relatively small extent on the pressure of the gas. Since the results of this experiment (in which the measuring system contained phosphorus pentoxide in close proximity to the graphite bulb) agree well with those of later ones (in which the measuring system contained no pentoxide), it follows that little water, if any, was disengaged during the reaction between the oxygen and the hydrogenated graphite. The highest sorption-value recorded represents about 4% of the hydrogen which had been driven into the graphite.

IV. Vacuum-heating for 72 hours now yielded some 200 c.mm. of permanent gas. Following this treatment the activity of the graphite towards oxygen was redetermined without further addition of hydrogen. The results, given in column D together with those calculated from the equation $s = 7{\cdot}8 \,.\, t^{0{\cdot}190}$ indicate that, whilst the graphite was considerably more active than it had been originally, the greater part of its " induced " activity had been lost.

V. After a further protracted period of vacuum-heating the activity of the graphite towards carbon dioxide was tested both before and after the further addition of 2·3 c.c. (N.T.P.) of hydrogen under the influence of the discharge. The results of these experiments, which appear in columns E and F of the table, indicate that

the hydrogen, whilst perhaps exerting catalytic activity, had little influence on the amount of carbon dioxide ultimately taken up. Towards the end of the second experiment (hydrogen present in the

TABLE I.

Sorption values are expressed in cubic millimetres at N.T.P.

	Oxygen. Hydrogen absent.				Oxygen. Hydrogen present.				Carbon dioxide.	Oxygen.
	Initial.		Repeat.		Initial.		Repeat.		Hydrogen.	Hydrogen.
Time (mins.).	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Absent.	Present.	Present.
	A.		B.		C.		D.		E.	F.	G.
1	1·9	2·9	2·7	2·7	34	34	4·9	7·8	1·9	4·5	—
2	3·6	3·3	3·5	3·1	39	39	6·9	8·9	2·0	5·4	—
3	3·6	3·6	—	—	42	42	—	—	2·0	5·7	34
4	—	—	3·7	3·5	45	44	—	—	2·4	6·2	—
5	4·3	4·0	—	—	47	46	8·9	10·6	—	6·2	39
6	—	—	—	—	48	48	—	—	—	—	41
8	—	—	—	—	51	51	—	—	—	6·2	—
10	—	—	4·2	4·1	53	53	12·1	12·1	2·8	6·4	45
13	—	—	—	—	55	55	—	—	—	—	—
15	—	—	4·2	4·4	57	57	12·8	13·0	—	—	48
20	6·0	5·1	4·4	4·7	61*	62*	14·0	13·8	3·9	—	52
30	—	—	—	—	64	66	15·0	14·9	—	—	56
40	6·4	5·8	5·2	5·3	67	69	15·7	15·7	5·7	—	59
50	—	—	—	—	69	72	—	—	—	—	61
60	—	—	—	—	—	—	17·1	17·0	—	—	63
70	6·7	6·6	—	—	73	77	—	—	—	—	65
80	—	—	5·7	6·1	—	—	17·9	17·9	6·7	—	69
100	7·3	7·0	—	—	77	81	—	—	6·8	6·4	72
150	7·5	7·5	—	—	85	89	20·1	20·5	—	—	79
200	7·9	7·9	6·2	7·1	91	93	—	—	—	—	83
240	—	—	—	—	95	96	—	—	—	—	88
290	8·5	8·5	—	—	99	100	—	—	—	—	—
320	—	—	—	—	101	102	—	—	—	—	—
1160	—	—	—	—	—	—	32·0	30·0	8·6	7·8	—
1350	—	—	—	—	127	133	—	—	—	—	—

* In these cases *et seq.*, the time ordinates should read as follows: 23, 33, 43, . . . 1353.

graphite), a bulb which formed part of the measuring system was cooled in liquid air; the carbon dioxide could thus be recovered quantitatively from the graphite without heating, and, further, no carbon monoxide (or any other permanent gas) had developed in the system from the reducing action of the atomic hydrogen.

VI. Following the removal of carbon dioxide in the cold, the activity of the graphite towards oxygen was again determined; the results are given in column G of the table and will be referred to later.

It will be noticed that the equations used to obtain the calculated sorption values for oxygen all involve a common power of t, *viz.*, $t^{0\cdot190}$. This fact (which implies a constancy of ratio between the different s-values for equal times) is most surprising, since a

growing mass of evidence obtained in these laboratories points to the conclusion that whilst equations of the type $s = k \cdot t^b$ are applicable in a large number of cases of sorption, the index b is highly susceptible to changes in the past history of the solid, and to the presence or otherwise of minute amounts of impurity. It is indeed difficult to escape the conclusion that the original activity of the graphite towards oxygen was due more or less directly to the hydrogen which it contained on manufacture.

The Variation of the "Induced" Activity with the Amount of Absorbed Hydrogen.

Experiments were next carried out to determine the quantitative relation between the amounts of hydrogen driven into the graphite and the consequent "induced" activities of the solid towards oxygen. In order to eliminate as a variant the pressure of the oxygen, the original calibrated deadspace was replaced by a graduated burette connected at its lower end by rubber tubing to a mercury reservoir. As the gas disappeared, its pressure was maintained by raising the level of the mercury in the burette, the McLeod gauge serving mainly as a null instrument.

Since the hydrogen, once driven into the graphite, could not again be removed, it was necessary to use a fresh specimen of the powder for each experiment. In spite of the exercise of scrupulous care to ensure uniform vacuum-heat treatment for the different specimens, and of their withdrawal from a common stock of the ground-up material which had been thoroughly mixed, they showed remarkable differences in their original behaviour towards oxygen. For this reason, it was necessary to determine with some care the original activity of each sample.

The cause of this variation of original activity could not be traced. Experiments on separate samples of graphite, wherein the only known variant was the duration of the vacuum-heating, seemed to indicate that prolonged treatment reduced the activity towards oxygen. The "normal" treatment of 72 hours led to sorption values about 10% lower than those obtained after only 24 hours' vacuum-heating. On two occasions where the preliminary experiments yielded abnormally high sorption values, a repetition of the vacuum-heating gave normal results.

Seven series of experiments were carried out, the same quantity of graphite being used in each case, and the amounts of added hydrogen varying from 531 to 5290 c.mm. The detailed results of one of these, given in Table II below, will serve to illustrate the agreement between the observed sorption-values and those calculated from the equation $s = k \cdot t^{0{\cdot}190}$.

TABLE II.

Sorption values are expressed in cubic millimetres (N.T.P.).

Time (mins.).	Preliminary experiment. No added hydrogen.		Final experiment. 5290 c.mm. (N.T.P.) of hydrogen added.	
	s obs.	*s* calc.	*s* obs.	*s* calc.
1	0·9	1·2	47	50
2	1·2	1·3	57	57
3	1·4	1·4	62	62
4	1·6	1·5	65	65
5	1·7	1·6	68	68
7	1·8	1·7	73	73
10	2·0	1·8	78	78
15	2·1	1·9	85	84
20	2·2	2·0	88	89
30	2·3	2·2	98	96
40	2·3	2·3	103	102
50	2·4	2·4	105	106
70	2·5	2·6	114	113
100	2·6	2·8	122	121
150	2·8	3·0	131	131
200	3·0	3·1	—	—

In the absence of equilibrium data (presumably unattainable), the factor k forms the best available basis for comparing the activities of the graphite in the different experiments. The *increase* in the value of k, following the absorption of a given quantity of hydrogen, affords similarly a measure of the "induced" activity. In Table III these increments $(k_2 - k_1)$ are compared with the amounts of added hydrogen (v in c.mm. at N.T.P.), and it is seen that the ratio $(k_2 - k_1)/v$ is nearly constant. The "induced" activity of the graphite is thus directly proportional to the amount of hydrogen driven into the graphite.

TABLE III.

v.	k_1. Before addn.	k_2. After addn.	$(k_2-k_1)/v$.	v.	k_1. Before addn.	k_2. After addn.	$(k_2-k_1)/v$.
531	0·9	5·2	0·0080	3675	3·5	37·3	0·0090
1062	6·3	13·7,	0·0070	5290	7·0	41·3	0·0065
1856	5·3	19·6	0·0077	5290	1·2	50·1	0·0092
2645	1·9	22·4	0·0077				

The low value for the ratio $(k_2 - k_1)/v$ yielded by the penultimate series is undoubtedly connected with a modification of the normal procedure on that occasion, the graphite being allowed to stand over-night with the bulk of the hydrogen absorbed in it, and a small residue being added the next day before the oxygen sorption experiment.* That the "induced" activity of the graphite does slowly

* The normal procedure was to carry out the hydrogen absorption continuously, and to test the activity of the graphite towards oxygen on the same day.

decay was proved by a special experiment designed to test the point. At high temperatures, the decay is probably more rapid. On the other hand, the rate of decay appears to depend considerably on other circumstances, as is exemplified by the results of expt. VI. Although the full period of the carbon dioxide experiment (*ca.* 24 hours) elapsed between the absorption of hydrogen and the activity test with oxygen, the results of the latter, compared with those of the previous oxygen experiment, represent an increase of activity which corresponds exactly to the quantity of hydrogen absorbed. The ratio $(k_2 - k_1)/v$ amounts in this case to 0·0091.

Experiments in which the amount of graphite taken varied from 0·34 to 13 g. led to the conclusion that, at any rate between these limits, the " induced " activities were independent of the amount of the solid, and dependent only on the quantity of added hydrogen. Nevertheless, there are several objections to the view that the part played by the carbon is simply to maintain the hydrogen in its reactive state, so that it can combine with oxygen on admission of the latter. These are :

(1) Little water, if any, is disengaged during the process of the sorption, while on the other hand there is definite evidence that, on heating the " activated " material after prolonged exposure to oxygen, considerably more gas is evolved than if the exposure to oxygen is omitted.

(2) The " original " activity displays characteristics identical with those of the " induced " activity.

(3) The " original " activity of the graphite is reproducible (almost quantitatively) simply by submitting it to vacuum-heating.

(4) A specimen of Acheson graphite which had been exposed to the air for some years showed much the same (average) " original " activity as one fresh from the makers.

A simple explanation of the effect of the hydrogen-bombardment arises from a consideration of the crystal structure of graphite as determined by the *X*-ray method. According, for example, to Bernal (*Proc. Roy. Soc.*, 1924, *A*, **106**, 749), the carbon atoms lie in planes of successive nets of hexagons in such a way that whilst in any one plane they are extremely densely packed, the distance between successive planes is relatively great. The high degree of mutual saturation of the atoms in any one plane (comparable with that in benzene) renders the field between adjacent planes extremely weak, and hence it is that graphite is a poor " sorbent " and a good lubricant. We shall suppose that, unlike ordinary molecular hydrogen, the ions H^+ and H_2^+, projected with great energy against

the solid particles, are capable of entering into combination with the carbon to form C_xH_y. The mutual saturation of the carbon–carbon bonds being thereby destroyed, the absorption of hydrogen should effect somewhat similar changes of properties to those which accompany the reduction of benzene to dihydrobenzene. Absorption of H_2^+ would lead, in fact, to the formation of linkings of the ethylenic type, and that of isolated H^+ ions—if it occurred—to a still higher degree of unsaturation. Thus regarded, the fact that exposure to oxygen does not lead immediately to the formation and elimination of water need occasion no surprise, since the oxygen atoms would tend to add themselves to pairs of unsaturated carbon atoms.* The slow decay of the "induced" activity may reasonably be attributed to the tendency of the unsaturated carbon atoms to form conjugate systems.

The work of Debye and Scherrer (*Physikal. Z.*, 1917, **18**, 291) and of Asahara (*Japan J. Chem.*, 1922, **1**, 35) has made it clear that amorphous carbon (so-called) is essentially an agglomerate of extremely minute crystals which are graphitic in structure. The hydrogen content is, however, much greater than in graphite, and, quite apart from the question of its porosity, the greater sorptive activity of this substance is fully to be expected. The fact that the activities of different charcoals increase with their hydrogen content has been established by H. H. Lowry (*J. Amer. Chem. Soc.*, 1924, **46**, 824). If the above explanation is correct, it is clear that the activity produced by a given proportion of hydrogen will depend very largely on its manner of distribution; also that many substances other than hydrogen should be capable of influencing the activity. The remarkable differences in "original" activity of the specimens of graphite indeed suggest that the activation could be brought about by other and simpler means than bombardment with hydrogen ions.

The possible influence of the gases (other than hydrogen) remaining sorbed in the graphite after its 72 hours' vacuum-heating has not been considered. Supposing these to consist largely of oxygen, it might be thought that the function of the hydrogen ions was simply to cause the removal of this as water, and so to permit a further quantity of oxygen to be taken up by the graphite on its exposure to that gas. It is certain, however, that no water or other

* The question of the location, with respect to the surface of the solid, of the sorbed molecules in cases where the sorption obeys the formula $s = k \cdot t^b$ will be discussed in a future paper, together with that of the probable significance of this equation. It may be remarked, however, that the equation appears characteristic of "sorption" processes involving definite chemical reactions (such as are here considered) and not of the condensation in capillary spaces of vapours approaching saturation.

volatile substance was given off during the hydrogen-bombardment, since, on stopping the discharge and pumping out the deadspace hydrogen, no detectable gas whatsoever developed in the system on standing over long periods. Any water formed must, in fact, have been bound to the carbon complex about as tightly as its elements are in the case, for example, of the sugars. In some way or other, therefore, the primary valencies of the carbon atoms must be called upon, and the organic analogy would suggest that the first explanation is correct. The relatively gross quantities of hydrogen absorbed by the graphite under the discharge also warrant the conclusion that the absorption is due to direct combination with the carbon atoms.

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CLII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXV. Three Optically Active Alcohols containing a Phenyl Group and some Esters derived therefrom.*

By LESLIE FRANK HEWITT and JOSEPH KENYON.

OF the optically active secondary alcohols that have already been examined, seven only have contained an aromatic radical. In optical properties, these seven alcohols contrast in several respects with alcohols of purely aliphatic character, and it was considered advisable to extend their number. Three optically active alcohols have therefore been prepared each containing a phenyl group, namely, β-phenylethylethylcarbinol, β-phenylethyl-*n*-propylcarbinol, and phenyl-β-phenylethyl carbinol. One of the most pronounced differences between an optically active alcohol containing a phenyl group and the corresponding aliphatic alcohol containing the same number of carbon atoms is that the rotatory powers of the former class are much greater than those of the latter. It may be noted, however, that the farther the phenyl group is removed from the asymmetric carbon atom in the following series of compounds, the smaller becomes its enhancing effect on the rotatory power.

Molecular Rotatory Powers, $[M]_D^{20°}$.

*$CH_3 \cdot CH(OH) \cdot Ph$	50·9°	*$CH_3 \cdot CH(OH) \cdot CH_2Ph$.....	36·1°
†$CH_3 \cdot CH(OH) \cdot C_6H_{13}(n)$	12·7	†$CH_3 \cdot CH(OH) \cdot CH_2 \cdot C_6H_{13}(n)$	12·9
	38·2		23·2
*$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2Ph$	21·3*		
†$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot C_6H_{13}(n)$	13·7		
	7·6		
*$CH_3 \cdot CH_2 \cdot CH(OH) \cdot Ph$	35·2°		
‡$CH_3 \cdot CH_2 \cdot CH(OH) \cdot C_6H_{13}(n)$	10·6		
	24·6		
$CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH_2Ph$	31·0°		
‡$CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot C_6H_{13}(n)$	10·7		
	20·3		

* Data given in Part VI, J., 1914, **105**, 1123. † In Part I, J., 1911, **99**, 49.
‡ In Part IV, J., 1913, **103**, 1933.

Two further interesting points of difference arise when comparisons are made of the optical rotatory dispersions of these two series of alcohols. In the first place, the values of the rotatory dispersion $\alpha_{4358}^{20°}/\alpha_{5461}^{20°}$ for the members of the aliphatic series of alcohols are almost constant, lying between the narrow limits 1·63 and 1·66, whilst the corresponding values for members of the aromatic series of alcohols vary between 1·53 and 1·83. Furthermore, whilst the rotatory dispersions of the former class of compounds are only slightly affected by changes of temperature, those of the latter are very susceptible to this influence.

These aromatic alcohols show complex rotatory dispersion, since their rotatory powers cannot be expressed by a Drude equation of one term.

The absorption spectra of many aromatic compounds have been investigated (Baly, J., 1908, **93**, 1902), and in almost every case the spectra are described as being of some complexity and as containing at least one band nearer to the visible portion of the spectrum than $\lambda = 2500$ Å.U. An absorption band in this position corresponds, in a substance of simple dispersion, to a dispersion ratio $\alpha_{4358}/\alpha_{5461}$ of at least 1·85.* In the following table are given the values of this dispersion ratio for a number of aromatic secondary alcohols, and it will be observed that these all lie below this value. This is particularly the case with the alcohol which contains two phenyl groups in the molecule.

* When $\lambda_0 = 0{\cdot}25$, $\lambda_0^2 = 0{\cdot}0625$ and $\alpha_{4358}/\alpha_{5461} = (0{\cdot}5461^2 - 0{\cdot}0625)/(0{\cdot}4358^2 - 0{\cdot}0625) = 1{\cdot}85$. It should be pointed out, however, that this calculation involves the assumption that the band of greater wave-length than $\lambda = 2500$ is a rotatory absorption band and not one which controls only the refractive dispersion.

Dispersion ratios ($\alpha_{4358}/\alpha_{5461}$) *at 20° for the alcohols in the homogeneous state.*

Phenylmethylcarbinol	1·736	β-Phenylethylethylcarbinol ...	1·695
Phenylethylcarbinol	1·687	β-Phenylethyl-*n*-propylcarbinol	1·757
Benzylmethylcarbinol	1·833	Phenyl-β-phenylethylcarbinol	1·533
β-Phenylethylmethylcarbinol	1·670		

A number of esters of the three optically active alcohols have been prepared and, in addition, three from *d*-β-phenylethylmethylcarbinol for purposes of comparison. The values of the rotatory dispersion ratio $\alpha_{4358}/\alpha_{5461}$ of these esters lie between the limits 1·78 and 2·51, except in the case of β-phenylethylmethylcarbinyl acetate, which has the very low value of 0·2 at 20°.

Experimental.

β-*Phenylethylethylcarbinol* (α-*Phenyl-γ-pentanol*).—A mixture of propionic and β-phenylpropionic acids was slowly passed over thoria at 420° and after removal of unchanged acids the resulting mixture of ketones was fractionally distilled. The phenylpentanone (b. p. 140°/14 mm.) thus obtained was reduced with sodium in moist ethereal solution, when the corresponding carbinol was readily obtained in good yield.

dl-β-*Phenylethylethylcarbinyl hydrogen phthalate* was obtained by heating a mixture of the carbinol and phthalic anhydride in molecular proportions at 110° for 15 hours and purifying the product in the usual manner. It crystallised from acetic acid in white prisms, m. p. 74°. 0·3996 G. required for neutralisation 29·3 c. c. of 0·0436*N*-NaOH; calc., for $C_{19}H_{20}O_4$, 29·35 c.c.

d- and l-β-*Phenylethylethylcarbinyl Hydrogen Phthalates*.—The *strychnine* salt of the *dl*-hydrogen phthalic ester was systematically crystallised from methyl alcohol–acetone. After six crystallisations, the strychnine salt *l*-B, *d*-A was obtained in a condition of optical purity: m. p. 158°, $[\alpha]_{5461}$ — 38·7° ($c = 5\%$ in chloroform solution). The more soluble fractions of the strychnine salt gave on decomposition a partly active hydrogen phthalic ester as a pasty mass which had $[\alpha]_{5461}$ — 15° in ethyl-alcoholic solution. Careful fractional crystallisation of this product from benzene–light petroleum yielded as the more soluble component a hydrogen phthalic ester with $[\alpha]_{5461}$ — 35° in ethyl-alcoholic solution. Five crystallisations from acetone of the *cinchonidine* salt of this highly active ester yielded the optically pure salt *l*-B, *l*-A in small, ill-defined crystals, m. p. 154°, which show $[\alpha]_{5461}$ — 54·2° ($c = 5\%$ in ethyl-alcoholic solution).

The *d*- and *l*-hydrogen phthalic esters were recovered from their corresponding alkaloidal salts in the form of colourless, viscous

gums which could not be induced to crystallise even when inoculated with the *dl*-ester of m. p. 74°. They show $[\alpha]_{5461} \pm 42{\cdot}9°$ ($c = 5\%$ in ethyl-alcoholic solution).

d- and l-β-*Phenylethylethylcarbinols* were obtained by heating the hydrogen phthalic esters with caustic soda solution and passing a current of steam. They distil at 143°/19 mm. and melt at 38°, whereas the *dl*-alcohol is a liquid.

β-*Phenylethyl*-n-*propylcarbinol* (α-*Phenyl*-γ-*hexanol*).—A mixture of *n*-butyric and β-phenylpropionic acids was passed over thoria at 425°. The phenylhexanone (b. p. 150°/20 mm.) isolated from the reaction mixture was reduced with sodium and moist ether, when the corresponding carbinol was obtained in good yield.

dl-β-*Phenylethyl*-n-*propylcarbinyl hydrogen phthalate*, obtained as described above, crystallises readily from many organic solvents in triangular prisms, m. p. 108°. 0·6343 G. required 21·8 c.c. of 0·0886*N*-NaOH; calc. for $C_{20}H_{22}O_4$, 21·9 c.c.

d- and l-β-*Phenylethyl*-n-*propylcarbinyl Hydrogen Phthalates*.—Fractional crystallisation of the very soluble *brucine* salt of the *dl*-hydrogen phthalic ester ten times from acetone gave the pure *l*-B, *l*-A salt, m. p. 95°, which has $[\alpha]_{5893} - 2{\cdot}1°$ ($c = 5\%$ in ethyl-alcoholic solution). Decomposition of the more soluble fractions of the brucine salt gave a partly active dextrorotatory hydrogen phthalic ester which after crystallisation from acetic acid gave as the more soluble fraction an acid ester of high dextrorotation. The crystallisation five times from acetone of the *brucine* salt of this dextrorotatory acid ester yielded the optically pure *l*-B, *d*-A salt, m. p. 75°, which shows $[\alpha]_{5893} - 12{\cdot}5°$.* The *l*- and *d*-hydrogen phthalic esters obtained from the respective brucine salts melt at 75° and have $[\alpha]_{5893} \pm 25{\cdot}5°$.

d- and l-β-*Phenylethyl*-n-*propylcarbinols* are volatile in steam, distil at 146°/16 mm., and form stellate clusters of prismatic needles, m. p. 34°. When crystals of the *d*- and *l*-carbinols are mixed, a liquid results.

Phenyl-β-*phenylethylcarbinol* (αδ-*Diphenyl*-α-*propanol*) has been described by Perkin (J., 1890, **59**, 1008) and by Harries and Hübner (*Annalen*, 1897, **296**, 325). A method based on that of the latter workers has been employed; benzylideneacetophenone in ethyl-

* The curious observation was made that the rotatory powers of the *l*-brucine salt of the *d*-acid ester were of a higher lævorotation than those of the *l*-brucine salt of the corresponding *l*-acid ester. The following determinations were made in alcoholic solution ($c = 5\%$):

Salt.	$[\alpha]_\lambda$ 5893°	5461°	4358°	$\alpha_{4358}/\alpha_{5461}$
l-B, *l*-A	− 2·1°	− 3·6°	−20·6°	5·7
l-B, *d*-A	−12·5	−15·1	−38·6	2·5

alcoholic solution was reduced with sodium amalgam, hydrochloric acid being run in continuously to maintain the alkalinity at a minimum. A poor yield, never exceeding 25%, was obtained together with considerable quantities of the corresponding pinacol.

The carbinol (b. p. 200°/20 mm.) was obtained as a pale yellow, viscous oil containing a coloured impurity which is not easily removed by distillation. As mentioned later, it has been obtained as a white solid by hydrolysis of its purified hydrogen phthalic ester.

dl-*Phenyl*-β-*phenylethylcarbinyl hydrogen phthalate* was obtained by the method outlined above, as a white solid which crystallises from acetic acid in small, rectangular prisms, m. p. 110°. 0·4417 G. required 13·8 c.c. of 0·0886*N*-NaOH; calc. for $C_{23}H_{20}O_4$, 13·85 c.c.

d- and l-*Phenyl*-β-*phenylethylcarbinyl Hydrogen Phthalates.*—Five crystallisations from acetone of the *brucine* salt of the *dl*-ester yielded the pure *l*-B, *l*-A salt in hard, rectangular prisms, m. p. 121°, which show $[\alpha]_{5893}$ — 8·8° (c = 5% in ethyl-alcoholic solution). The hydrogen phthalic ester recovered from the more soluble fractions of the brucine salt was converted into the corresponding *strychnine* salt. Fractional crystallisation of this salt five times from methyl alcohol rendered it optically pure. It forms hard needles, m. p. 189°, which are too insoluble in cold solvents for determinations of rotatory power to be made. The *d*- and *l*-hydrogen phthalic esters were obtained as viscous gums ($[\alpha]_{5893}$ ± 8·9°) which could not be induced to crystallise.

d- and *l-Phenyl*-β-*phenylethylcarbinols* are not volatile in steam. Each distils at 195°/15 mm. and sets to a white, crystalline mass, m. p. 54°. Equal weights of the two carbinols were melted together and allowed to cool; the resulting inactive carbinol melted at 45·5° to a colourless liquid.

Esters of the Optically Active Alcohols.—The esters of the alcohols with fatty acids were prepared as follows: the *formates*—by heating the alcohol with excess of formic acid for ½ hour at 100°; *acetates* and *propionates*—by heating the alcohol with a molecular quantity of acetic or propionic anhydride, respectively, at 100° for an hour.

The alcohols recovered from each ester by hydrolysis were of unchanged rotatory power in each case.

Determination of the Physical Constants.—The determinations of density, made in a pyknometer of about 1·5 c.c. capacity, are given in Table V. All determinations of rotatory power of substances in the homogeneous state were made with a polarimeter fitted with a direct-vision spectroscopic eyepiece, the optically active liquid being contained in a 50 mm. jacketed tube, around which mineral oil was circulated. The following light sources were used: sodium and lithium flames and an enclosed mercury arc.

The figures given in Tables I and IV are taken from smooth curves obtained from the experimental figures given in Tables V and VI. The photographic determinations of rotatory power were obtained by using an open iron arc. A neon lamp and an open copper arc were used, in addition to the above-mentioned light sources, for the measurement of refractive indices.

Table I.

Specific Rotatory Powers of the Alcohols in the Homogeneous State at Different Temperatures.

Temp.	d_4^t.	$[\alpha]_\lambda$. 6708.	5893.	5780.	5461.	4358.
		d-β-Phenylethylethylcarbinol.				
20°	0·9687	—	+18·95°	—	+23·00°	+38·98°
140	0·8773	—	18·70	—	23·30	39·98
		l-β-Phenylethyl-*n*-propylcarbinol.				
20°	0·9565	− 9·66°	−12·54	−13·18°	−15·06	−26·46*
140	0·8590	9·90	12·57	13·39	15·37	27·48
		d-Phenyl-β-phenylethylcarbinol.				
20° †	1·0661	+12·20	+16·12	+16·66	+18·95	+29·05
140	0·9640	14·87	18·63	19·34	21·68	35·16

* The following rotatory powers were determined at 20° by the photographic method: $[\alpha]_{4342}$ −27·1°, $[\alpha]_{4132}$ −31·4°, $[\alpha]_{3950}$ −35·6°, $[\alpha]_{3800}$ −39·7°.

† Certain of the values at 20° are extrapolated owing to the high melting point (54°) of the carbinol.

Table II.

Specific Rotatory Powers in Various Solvents at Room Temperature.

Solvent.	Grams of solute in 100 c.c. of solution.	$[\alpha]_\lambda$. 6708.	5893.	5780.	5461.	4358.
		d-β-Phenylethylethylcarbinol.				
Benzene	4·8	—	—	—	+29·7°	+51·1°
Ethyl alcohol ...	5·0	—	26·8°	—	31·8	55·4
Carbon disulphide	5·2	—	30·2	—	35·4	62·9
		d-β-Phenylethyl-*n*-propylcarbinol.				
Benzene	4·9	+12·2°	+14·9	+16·3°	+17·6	+31·6
Ethyl alcohol ...	5·1	—	17·3	18·8	20·7	37·4
Carbon disulphide	5·2	—	21·9	22·7	25·0	46·2
		l-Phenyl-β-phenylethylcarbinol.				
*cyclo*Hexane	5·0	−15·3	−20·2	−20·8	−23·1	−38·0
Ethyl alcohol ...	4·6	−12·3	−15·6	−16·2	−17·9	−28·6
Carbon disulphide	4·8	−19·7	−25·4	−26·5	−30·4	−49·1
		l-β-Phenylethyl-*n*-propylcarbinyl hydrogen phthalate.				
Ethyl alcohol ...	4·6	—	−25·5	—	−30·1	−57·1
Chloroform	4·8	—	−18·2	—	−21·6	−39·6
Carbon disulphide	4·6	—	−39·8	—	−48·0	−93·1
		l-Phenyl-β-phenylethylcarbinyl hydrogen phthalate.				
Ethyl alcohol ...	5·1	− 7·6	− 9·0	− 9·8	− 10·4	− 9·8
Methyl alcohol ...	4·8	− 9·9	−12·1	−13·1	− 13·8	− 17·7
Chloroform	4·3	−20·0	−25·7	−26·2	− 30·6	− 49·3
Carbon disulphide	4·0	−72·0	−92·5	−96·5	−112·3	−209·0

Table III.

Refractive Indices of *l*-β-Phenylethyl-*n*-propylcarbinol at 20°.

λ ...	6708	5896	5790	5782	5461	5218	5153	5106	4358
$n_{\lambda}^{20°}$	1·5041	1·5085	1·5093	1·5093	1·5118	1·5139	1·5147	1·5151	1·5258

Table IV.

Temp.	$d_{4}^{t°}$.	$[M]_{\lambda}$. 6708.	5893.	5780.	5461.	4358.
d-β-Phenylethylmethylcarbinyl formate, b. p. 120°/15 mm.						
20°	1·0083	−25·10°	−35·50°	−37·09°	−42·90°	−81·56°
140	0·9119	−27·06	−36·92	−38·23	−43·90	−82·95
d-β-Phenylethylmethylcarbinyl acetate, b. p. 130°/15 mm.						
20	0·9854	+ 2·92	+ 3·12	+ 3·14	+ 3·30	+ 0·63
140	0·8860	0·96	0·00	− 0·04	− 0·22	− 3·96
d-β-Phenylethylmethylcarbinyl propionate, b. p. 141°/16 mm.						
20	0·9790	− 3·21	− 5·97	− 6·22	− 8·08	−20·23
140	0·8792	− 3·48	− 6·03	− 6·34	− 9·03	−21·61
d-β-Phenylethylethylcarbinyl formate,* b. p. 135°/15 mm.						
20	0·9980	−32·74	−43·98	−46·33	−52·59	−98·34
140	0·8980	−27·88	−38·40	−40·62	−48·02	−86·38
d-β-Phenylethylethylcarbinyl acetate,† b. p. 147°/19 mm.						
20	0·9829	−28·31	−38·27	−40·19	−46·76	−87·38
140	0·8825	−23·77	−31·29	−33·43	−38·67	−70·37
l-β-Phenylethylethylcarbinyl propionate, b. p. 150°/14 mm.						
20	0·9731	+33·84	+46·11	+47·83	+55·31	+101·64
140	0·8703	26·99	35·90	37·16	43·63	78·98
l-β-Phenylethyl-*n*-propylcarbinyl formate,‡ b. p. 147°/18 mm.						
20	0·9872	+34·52	+45·87	+47·98	+55·64	+101·70
140	0·8959	29·20	38·69	41·07	46·02	84·25
l-β-Phenylethyl-*n*-propylcarbinyl acetate, b. p. 154°/20 mm.						
20	0·9725	+26·91	+36·65	+38·15	+43·34	+79·60
140	0·8750	22·37	29·77	30·98	35·55	61·93
d-β-Phenylethyl-*n*-propylcarbinyl propionate, b. p. 163°/18 mm.						
20	0·9629	−28·94	−38·66	−40·72	−46·80	−85·82
140	0·8688	−23·52	−31·26	−32·88	−37·34	−67·16
d-Phenyl-β-phenylethylcarbinyl formate, b. p. 195°/15 mm.						
20	1·0790	+68·16	+92·16	+96·79	+110·76	+196·80
140	0·9741	59·35	81·55	84·10	94·32	166·25
d-Phenyl-β-phenylethylcarbinyl acetate, b. p. 165°/2 mm.						
20	1·0670	+103·3	+139·1	+144·7	+166·8	+297·8
140	0·9672	103·8	141·5	146·6	167·4	302·1

Additional Photographic Determinations at 20°.

* $[M]_{4310}$ −100·8°; $[M]_{4145}$ −112·3°; $[M]_{4035}$ −123·9°; $[M]_{3915}$ −135·4°.
† $[M]_{4226}$ −89·9°; $[M]_{3950}$ −119·5°; $[M]_{3850}$ −128·1°.
‡ $[M]_{4310}$ +106·4°; $[M]_{4190}$ +114·9°; $[M]_{4057}$ +127·6°; $[M]_{3925}$ +140·4°.

Table V.

Densities of Alcohols and Esters.

d-β-Phenylethylethylcarbinol (in fused state).
d_4^t 0·9485 at 46·3°; 0·9288 at 72·5°; 0·9074 at 100·5°; 0·8832 at 131·5°.

l-β-Phenylethyl-*n*-propylcarbinol (in fused state).
d_4^t 0·9588 at 17°; 0·9281 at 56·5°; 0·8982 at 93·3°; 0·8678 at 129·3°.

d-Phenyl-β-phenylethylcarbinol (in fused state).
d_4^t 1·0228 at 70°; 1·0068 at 88·5°; 1·0046 at 92·5°; 0·9856 at 115°.

d-β-Phenylethylmethylcarbinyl formate.
d_4^t 1·0132 at 14·5°; 0·9849 at 49·5°; 0·9553 at 86°; 0·9330 at 114·5°.

d-β-Phenylethylmethylcarbinyl acetate.
d_4^t 0·9874 at 17°; 0·9451 at 68·5°; 0·9249 at 91°; 0·9042 at 117·5°.

d-β-Phenylethylmethylcarbinyl propionate.
d_4^t 0·9851 at 13°; 0·9348 at 72°; 0·9194 at 91°; 0·8970 at 117°.

d-β-Phenylethylethylcarbinyl propionate.
d_4^t 0·9997 at 17·8°; 0·9681 at 55°; 0·9416 at 86°; 0·9088 at 126·5°.

d-β-Phenylethylethylcarbinyl acetate.
d_4^t 0·9863 at 15·3°; 0·9614 at 46°; 0·9256 at 88°; 0·8988 at 117·3°.

l-β-Phenylethylethylcarbinyl propionate.
d_4^t 0·9723 at 20·5°; 0·9450 at 52·3°; 0·9209 at 81°; 0·8851 at 123°.

l-β-Phenylethyl-*n*-propylcarbinyl formate.
d_4^t 0·9872 at 20·5°; 0·9606 at 56·5°; 0·9368 at 84·5°; 0·9209 at 105·5°.

l-β-Phenylethyl-*n*-propylcarbinyl acetate.
d_4^t 0·9803 at 10°; 0·9436 at 56·5°; 0·9179 at 87·5°; 0·8923 at 118·5°.

d-β-Phenylethyl-*n*-propylcarbinyl propionate.
d_4^t 0·9674 at 14·5°; 0·9397 at 49·5°; 0·9143 at 79·5°; 0·8920 at 109·5°.

l-Phenyl-β-phenylethylcarbinyl formate.
d_4^t 1·0821 at 16·4°; 1·0473 at 56·5°; 1·0226 at 85°; 1·0016 at 114·5°.

d-Phenyl-β-phenylethylcarbinyl acetate.
d_4^t 1·0709 at 15°; 1·0472 at 43°; 1·0198 at 78·5°; 0·9918 at 110°.

Table VI.

Observed Rotatory Powers in the Homogeneous State of a 50 mm. Layer of the Liquid.

d-β-Phenylethylethylcarbinol (in fused state).

α_{5893} +9·14° at 52·5°; 9·10° at 65°; 9·02° at 72°; 9·01° at 92·5°; 9·00° at 106·5°; 8·72° at 120·5°.

α_{5461} +11·09° at 52·5°; 11·08° at 64·5°; 11·06° at 72°; 11·01° at 93°; 10·99° at 106°; 10·73° at 121·5°; 10·26° at 139°.

α_{4358} +18·84° at 52·5°; 18·77° at 66°; 18·76° at 72°; 18·74° at 92·5°; 18·70° at 106°; 18·26° at 121°.

l-β-Phenylethyl-*n*-propylcarbinol (in fused state).

α_{6708} −4·64° at 22°; 4·70° at 45°; 4·57° at 88°; 4·35° at 120°; 4·24° at 142°.

α_{5893} −6·35° at 22°; 6·60° at 45°; 6·27° at 88°; 5·75° at 120°; 5·50° at 142°.

α_{5780} −6·35° at 22°; 6·60° at 45°; 6·53° at 89°; 6·04° at 120°; 5·75° at 142°.

α_{5461} −7·25° at 22°; 7·47° at 45°; 7·40° at 89°; 7·04° at 120°; 6·53° at 141°.

α_{4358} −12·73° at 22°; 13·12° at 49°; 13·00° at 89°; 12·52° at 120°; 11·69° at 141°.

TABLE VI *continued.*

d-Phenyl-β-phenylethylcarbinol (in fused state).

α_{6708} +6·99° at 62°; 7·35° at 88·5°; 7·55° at 106·5°; 7·43° at 120°.
α_{5893} +9·17° at 62°; 9·57° at 89·5°; 9·52° at 106·5°; 9·34° at 120°.
α_{5780}* +9·20° at 40°; 9·83° at 95·5°; 9·88° at 106·5°; 9·08° at 120°.
α_{5461}* +10·12° at 20°; 11·15° at 60°; 11·11° at 99°; 11·07° at 106·5°; 10·82° at 120°.
α_{4358}* +15·47° at 20°; 16·99° at 60°; 17·56° at 97°; 17·44° at 106·5°; 17·25° at 120°.

d-β-Phenylethylmethylcarbinyl formate.

α_{6708} −7·39° at 20°; 7·40° at 53°; 7·36° at 93°; 7·28° at 112°; 7·13° at 128°.
α_{5893} −10·05° at 20°; 10·13° at 54°; 10·01° at 93°; 9·87° at 114°; 9·68° at 127°.
α_{5780} −10·51° at 20°; 10·70° at 55°; 10·49° at 94°; 10·30° at 115°; 10·00° at 128°.
α_{5461} −12·16° at 20°; 12·35° at 54°; 12·12° at 95°; 11·77° at 116°; 11·48° at 128°.
α_{4358} −25·09° at 20°; 23·38° at 54·5°; 22·58° at 95°; 21·90° at 118°; 21·58° at 128°.

d-β-Phenylethylmethylcarbinyl acetate.

α_{6708} +0·75° at 16°; 0·60° at 63°; 0·45° at 96°; 0·40° at 112°; 0·36° at 120°.
α_{5893} +0·83° at 16°; 0·50° at 63°; 0·28° at 96°; 0·20° at 112°; 0·15° at 120°.
α_{5180} +0·84° at 16°; 0·47° at 63°; 0·27° at 96°; 0·18° at 112°; 0·10° at 120°.
α_{5461} +0·87° at 16°; 0·46° at 63°; 0·25° at 91°; 0·12° at 112°; 0·06° at 120°.
α_{4358} +0·16° at 16°; −0·35° at 63°; −0·57° at 90°; −0·75° at 112°; −0·82° at 120°.

d-β-Phenylethylmethylcarbinyl propionate.

α_{6708} −0·76° at 14°; 0·85° at 60°; 0·84° at 96°; 0·82° at 112°; 0·80° at 126°.
α_{5893} −1·38° at 14°; 1·40° at 60°; 1·44° at 96°; 1·37° at 112°; 1·32° at 126°.
α_{5780} −1·46° at 14°; 1·54° at 60°; 1·52° at 96°; 1·45° at 112°; 2·00° at 126°.
α_{4358} −4·76° at 14°; 4·98° at 60°; 5·00° at 96°; 4·90° at 112°; 4·78° at 126°.

d-β-Phenylethylethylcarbinyl formate.

α_{6708} −8·51° at 20°; 8·00° at 45°; 7·67° at 71·5°; 7·06° at 100°; 6·68° at 123°.
α_{5893} −11·43° at 20°; 10·90° at 46°; 10·30° at 71·5°; 9·61° at 100°; 9·02° at 123°.
α_{5780} −12·04° at 20°; 11·40° at 44·5°; 11·00° at 73·5°; 10·34° at 100°; 10·18° at 123°.
α_{5461} −13·93° at 20°; 13·16° at 44°; 12·66° at 71°; 11·91° at 100°; 11·50° at 123°.
α_{4358} −25·56° at 20°; 24·33° at 44·5°; 23·24° at 71°; 21·40° at 100°; 20·80° at 123°.

d-β-Phenylethylethylcarbinyl acetate.

α_{6708} −6·78° at 18·5°; 5·82° at 81°; 6·29° at 48°; 5·46° at 107°; 5·32° at 122°.
α_{5893} −9·19° at 18·5°; 8·54° at 48°; 7·80° at 81°; 7·42° at 107°; 7·08° at 122°.
α_{5780} −9·75° at 18·5°; 9·02° at 48°; 8·38° at 81°; 7·96° at 107°; 7·50° at 123°.
α_{5461} −11·20° at 18·5°; 10·59° at 48°; 9·84° at 81°; 9·12° at 107°; 8·64° at 125°.
α_{4358} −20·91° at 18·5°; 19·49° at 48°; 17·99° at 81°; 16·62° at 107°; 15·93° at 124°.

* These measurements were made with the supercooled liquid.

TABLE VI *continued*.

l-β-Phenylethylethylcarbinyl propionate.

a_{6708} +7·48° at 20°; 6·84° at 49°; 6·03° at 95°; 5·80° at 109°; 5·59° at 125°.
a_{5893} +10·20° at 20°; 9·28° at 49°; 8·68° at 77°; 8·16° at 96°; 7·38° at 125°.
a_{5780} +10·58° at 20°; 9·55° at 49°; 8·50° at 88°; 8·05° at 109°; 7·67° at 125°.
a_{5461} +12·23° at 20°; 11·05° at 49°; 9·86° at 92°; 9·40° at 109°; 9·00° at 125°.
a_{4358} +22·47° at 20°; 20·21° at 49°; 18·06° at 92°; 17·30° at 109°; 16·34° at 125°.

l-β-Phenylethyl-*n*-propylcarbinyl formate.

a_{6708} +8·08° at 19°; 7·82° at 37°; 7·31° at 70°; 6·80° at 109·5°; 6·54° at 124°.
a_{5893} +10·96° at 19°; 10·54° at 37°; 9·79° at 70°; 9·01° at 109·5°; 8·70° at 124°.
a_{5780} +11·46° at 19°; 10·29° at 70°; 9·58° at 98°; 9·51° at 109·5°; 9·21° at 124°.
a_{5461} +13·22° at 19°; 12·65° at 46°; 12·06° at 70°; 10·92° at 109·5°; 10·42° at 124°.
a_{4358} +24·28° at 19°; 23·06° at 43°; 21·78° at 70°; 19·77° at 109·5°; 19·02° at 124°.

l-β-Phenylethyl-*n*-propylcarbinyl acetate.

a_{6708} +5·98° at 17°; 5·38° at 66°; 5·12° at 71°; 4·80° at 108°; 4·62° at 129°.
a_{5893} +8·15° at 17°; 7·24° at 66°; 6·94° at 71°; 6·50° at 108°; 6·11° at 129°.
a_{5780} +8·50° at 17°; 7·61° at 66°; 7·20° at 71°; 6·76° at 108°; 6·32° at 129°.
a_{5461} +9·65° at 17°; 8·69° at 66°; 8·53° at 71°; 7·69° at 108°; 7·30° at 129°.
a_{4358} +17·73° at 17°; 15·68° at 66°; 15·07° at 71°; 14·03° at 108°; 12·84° at 129°.

d-β-Phenylethyl-*n*-propylcarbinyl propionate.

a_{6708} −6·03° at 16·4°; 5·23° at 64°; 5·01° at 88°; 4·69° at 112°; 4·55° at 124°.
a_{5893} −8·07° at 16·4°; 7·16° at 62°; 6·61° at 88°; 6·24° at 112°; 6·01° at 124°.
a_{5780} −8·48° at 16·4°; 7·59° at 61°; 7·02° at 89°; 6·54° at 112°; 6·33° at 124°.
a_{5461} −9·76° at 16·4°; 8·57° at 64°; 8·08° at 89°; 7·53° at 112°; 7·34° at 126°.
a_{4358} −17·88° at 16·4°; 15·95° at 62°; 14·37° at 87°; 13·60° at 112°; 13·19° at 125°.

l-Phenyl-β-phenylethylcarbinyl formate.

a_{6708} −15·48° at 14°; 14·43° at 60°; 13·85° at 83°; 13·16° at 105°; 12·66° at 123°.
a_{5893} −20·92° at 14°; 19·38° at 60°; 18·62° at 83°; 17·67° at 105°; 16·86° at 123°.
a_{5780} −21·90° at 14°; 20·40° at 60°; 19·60° at 83°; 18·52° at 105°; 17·92° at 123°.
a_{5461} −25·10° at 14°; 23·24° at 60°; 22·24° at 83°; 21·14° at 105°; 20·05° at 123°.
a_{4358} −44·75° at 14°; 40·75° at 60°; 38·87° at 83°; 36·88° at 105°; 35·28° at 123°.

d-Phenyl-β-phenylethylcarbinyl acetate.

a_{6708} +21·72° at 13°; 21·56° at 44°; 21·12° at 80°; 20·67° at 102°; 20·22° at 126°.
a_{5893} +29·29° at 13°; 28·95° at 43°; 28·40° at 79°; 27·96° at 102°; 27·36° at 125°.
a_{5780} +30·51° at 13°; 30·08° at 45°; 29·47° at 79°; 29·01° at 103°; 28·36° at 126°.
a_{5461} +35·13° at 13°; 34·67° at 45°; 33·97° at 79°; 33·37° at 104°; 32·47° at 127°.
a_{4358} +62·73° at 13°; 61·92° at 45°; 60·81° at 79°; 59·63° at 104°; 58·29° at 127°.

TABLE VII.

Refractive Indices of the Esters at 20° for Light of Various Frequencies.

	β-Phenylethylmethylcarbinyl			β-Phenylethylethylcarbinyl		
λ.	formate.	acetate.	propionate.	formate.	acetate.	propionate.
6708	1·4934	1·4968	1·4906	1·4298	1·4849	1·4809
6402	1·4946	—	1·4916	1·4944	1·4861	1·4821
6096	1·4965	—	1·4934	1·4962	1·4880	1·4838
5896	1·4978	1·5012	1·4947	1·4973	1·4890	1·4850
5882	1·4978	—	1·4947	1·4974	1·4890	1·4850
5790	1·4986	1·5021	1·4953	1·4979	1·4896	1·4856
5782	1·4986	1·5021	1·4954	1·4980	1·4896	1·4856
5700	1·4992	1·5026	1·4960	1·4985	1·4902	1·4861
5461	1·5011	1·5044	1·4978	1·5003	1·4920	1·4878
5218	1·5032	1·5068	1·4999	1·5024	1·4940	1·4898
5153	1·5040	1·5076	1·5006	1·5032	1·4947	1·4905
5106	1·5045	1·5081	1·5012	1·5037	1·4951	1·4909
4358	1·5153	1·5186	1·5113	1·5141	1·5051	1·5004
4046	1·5217	1·5253	1·5179	1·5204	—	1·5059

Refractive Indices of the Esters at 20°.

	β-Phenylethyl-*n*-propylcarbinyl			Phenyl-β-phenylethylcarbinyl	
λ.	formate.	acetate.	propionate.	formate.	acetate.
6708	1·4884	1·4824	1·4808	1·5526	1·5306
6402	1·4898	1·4832	1·4821	—	—
6096	1·4915	1·4849	1·4839	—	—
5896	1·4925	1·4863	1·4848	1·5584	1·5451
5882	1·4925	1·4863	1·4849	—	—
5790	1·4932	1·4870	1·4855	1·5590	1·5456
5782	1·4933	1·4870	1·4855	—	—
5700	1·4939	1·4877	1·4860	—	—
5461	1·4957	1·4894	1·4877	1·5624	1·5497
5218	1·4977	1·4915	1·4896	—	—
5153	1·4983	1·4921	1·4903	—	—
5108	1·4984	1·4926	1·4907	—	—
4358	1·5089	1·5019	1·5000	1·5818	1·5664
4046	1·5148	1·5079	—	1·5913	—

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CLIII.—*The Thermal Decomposition of Ammonia upon Various Surfaces.*

By CYRIL NORMAN HINSHELWOOD and ROBERT EMMETT BURK.

FROM the examples of hydrogen iodide (Bodenstein, *Z. physikal. Chem.*, 1899, **29**, 295), ozone (Chapman and Jones, J., 1910, **97**, 2463), chlorine monoxide (Hinshelwood and Prichard, J., 1923, **123**, 2730), and nitrous oxide (Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, *A*, **106**, 284), it is extremely probable that the thermal decomposition of ammonia would be bimolecular if it took place homogeneously. The homogeneous change has not been actually observed. In the experiments of Bodenstein and Kranendieck ("Nernst-Festschr.," 1912, p. 99), made in a vessel of quartz glass at 780° and 880°, the reaction observed was entirely a wall reaction, whilst in those of Perman and Atkinson (*Proc. Roy. Soc.*, 1904, **74**, 110), made in vessels of porcelain at higher temperatures, the nature of the observed reaction is not clear.

Recent experiments have shown that although the homogeneous decomposition of nitrous oxide is bimolecular, the catalytic decomposition on the surface of platinum and gold is unimolecular (Hinshelwood and Prichard, this vol., p. 327; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211), being resolved into the stages $N_2O = N_2 + O$, $2O = O_2$. In a similar way, it might be expected that, although the reaction $NH_3 = N + H + H_2$ or $NH_3 = N + 3H$ could not take place homogeneously, catalytically active surfaces would render it possible by adsorbing the atoms of hydrogen and nitrogen until they evaporate as molecules with others of their kind. There is abundant evidence of the affinity of metal surfaces for atomic hydrogen and oxygen. Nitrogen may well be similar in this respect.

We have made a study of the thermal decomposition of ammonia with the objects of finding whether the homogeneous reaction can be observed, and of investigating the kinetics of the catalytic reaction of various surfaces. The reaction was studied under the following conditions:

(*a*) In a vessel of fused silica at higher temperatures than those employed by Bodenstein and Kranendieck, up to 1050°.

(*b*) On the surface of a heated platinum wire, between 933° and 1215°.

(*c*) On the surface of a heated tungsten wire, between 631° and 941°.

In all cases equilibrium corresponds to almost complete decomposition of the ammonia. The general results of the investigation were as follows.

(1) Up to the highest temperature reached, 1050°, in a silica vessel, no sign of the homogeneous reaction was observed.

(2) The observations made on the reaction at silica surfaces were in general agreement with those of Bodenstein and Kranendieck, but the investigation of certain discrepancies between the two sets of observations led to some interesting conclusions about the mode of adsorption of ammonia, namely, that it is probably adsorbed on silica by means of its hydrogen atoms, and that the adsorption is very sensitive to the exact spacing of the silica molecules.

(3) Tungsten is the most efficient catalyst; the reaction at its surface is almost of zero order with respect to ammonia, and uninfluenced by the products of reaction. This catalyst is extremely constant in activity.

(4) The reaction on surfaces of platinum and silica is of the first order with respect to ammonia, and strongly retarded by hydrogen. The retarding influence of the hydrogen obeys a different law in the two cases. On platinum we have approximately

$$-d[NH_3]/dt = k[NH_3]/[H_2],$$

while on silica

$$-d[NH_3]/dt = k[NH_3]\{1 - c[H_2]\}.$$

(5) The retarded reaction on platinum has a very much greater temperature coefficient than the very much more rapid and unretarded reaction on tungsten, indicating that the temperature coefficient of the former reaction is largely determined by the freeing of the surface from hydrogen as the temperature increases.

Thermal Decomposition of Ammonia in a Silica Vessel.

A complete solution of the problem must elucidate the following points:

(1) The order of the reaction with respect to ammonia.

(2) The law according to which the retarding action of the products of reaction is exerted.

(3) The influence of temperature on the reaction velocity. In the ammonia decomposition, this appears to be a very complex matter. These points may be taken in order.

The experimental method was simply to measure the increase in pressure attending decomposition. In the experiments of Bodenstein and Kranendieck, corrections had to be made for the diffusion of hydrogen through the walls of the bulb. This was found unnecessary with the bulbs used in our experiments, partly because the actual diffusion of hydrogen per unit time was less and partly because the experiments nearly all occupied much less time.

The ordinary method of determining the order of a reaction is to find the influence of initial concentration upon the time required for the reaction to proceed to a given fraction of the way to completion. But when a reaction is retarded by the products, the order may easily be shown to be reduced owing to their influence. This may be explained as follows. Suppose the rate of decomposition to be expressed by the equation $dx/dt = k[NH_3]^n . f[\text{products}]$. Now if the products are very strongly adsorbed, so that the surface is almost completely covered as soon as their pressure attains quite a small value, then it can easily be shown that the amount of free surface where the ammonia can react is inversely proportional to the pressure of the products. Thus $dx/dt = k[NH_3]^n/[\text{products}]$. Integration of this equation shows that the observed order of the reaction would now be not n, but $n - 1$. Therefore, before assuming that the observed order of the reaction is actually the order with respect to ammonia we must know something about the degree of adsorption of the products.

The observed order of the reaction, obtained from the effect of initial pressure upon the time of half change, is nearly equal to one. This is illustrated by the following figures obtained when the bulb was in a fairly constant condition.

	T (abs.).	Initial pressure (mm.).	Time of half change (secs.).	T (abs.).	Initial pressure (mm.).	Time of half change (secs.).
Bulb I.	1264°	330	50	1220°	117	196
	1267	137·5	44	1220	298	191
	1268	325	57	1220	120	184
	1268	53·5	43			

The experiments are recorded in the order in which they were made. The same fact is illustrated by reading off the initial rate of reaction.

		Initial pressure. p_0.	$\left(\frac{\Delta p}{\Delta t}\right)_0$	$\frac{1}{p_0}\left(\frac{\Delta p}{\Delta t}\right)_0 \times 10^5$.		Initial pressure. p_0.	$\left(\frac{\Delta p}{\Delta t}\right)_0$	$\frac{1}{p_0}\left(\frac{\Delta p}{\Delta t}\right)_0 \times 10^5$.
Bulb II.	(1)	296	0·30	101	(2)	104	0·088	85
T (abs.).	(3)	259	0·24	93	(5)	92	0·075	82
1313°	(6)	239	0·19	80	(7)	75	0·073	97
	(4)	209	0·18	86				

The numbers in brackets indicate the order in which the determinations were made. The comparative constancy of the figures in the last column makes it clear that under these conditions the reaction can be regarded as empirically of the first order.

Retarding Influence of the Products.—Bodenstein and Kranendieck found that the products of the reaction had a retarding influence.

Our experiments confirmed this even at 1300° Abs. If the reaction products are strongly adsorbed from the very beginning of the reaction, then the observed order will be less than the true order with respect to ammonia. But in the equation $dx/dt = k[NH_3]^n f[\text{products}]$ we cannot, from observation of the velocity of the reaction at different points on the reaction–time curve, determine $f[\text{products}]$ unless we first know n. (Attempts to determine this function with any precision by determining the initial velocity of the reaction for a constant pressure of ammonia, and varying the pressure of nitrogen and hydrogen previously introduced, were frustrated by the variability of the bulb surface.) There is thus a vicious circle which can only be broken by a method resembling successive approximation. We assume first that the order of reaction determined empirically in the last section is the true order, namely, that n is 1. From the experimental values of p and t throughout a given experiment, we obtain values of $\Delta p/\Delta t$ over small ranges and the corresponding mean values of the pressures of ammonia and the products of the reaction. Then $1/p_{NH_3} . \Delta p/\Delta t$ is the rate of reaction corrected for the changing concentration of ammonia, assuming that n is 1. This is proportional to the surface left uncovered by the products of the reaction. We now plot $1/p_{NH_3} . \Delta p/\Delta t$ against the pressure of the products. Figure 1 illustrates the type of result found, the diminution of surface being almost a linear function of the pressure of the products over a very considerable range, indeed until the surface is reduced almost to zero. If $V = 1/p_{NH_3} . \Delta p/\Delta t$, then it follows that over a large range $V = V_0(1 - c[\text{products}])$. The following figures illustrate this: p = average pressure of the products, $V_{obs.} = \dfrac{1}{p_{NH_3}} \cdot \dfrac{\Delta p}{\Delta t} \times 1000$, and $V_{calc.}$ is calculated from the formula $V_{calc.} = 1{\cdot}35(1 - 0{\cdot}0054p)$.

p	12	32	52	72	86	101	121	141
$V_{obs.}$	1·31	1·08	1·02	0·85	0·69	0·61	0·50	0·32
$V_{calc.}$	1·27	1·11	0·97	0·86	0·74	0·63	0·47	0·32

The quantity $(1 - cp)$ gives the fraction of the surface left free for a given pressure of the products. The important observation was made that c was independent of the temperature. Thus the following values were obtained:

T (abs.)	1267°	1267°	1268°	1220°	1196°	1163°	1064°
$c \times 10^5$	455	455	375	435	423	540	418

Thus, under the conditions of these experiments, the retarding action of the products is independent of the temperature over a range of 200 degrees.

By assuming that n is 1, we have thus arrived at the equation

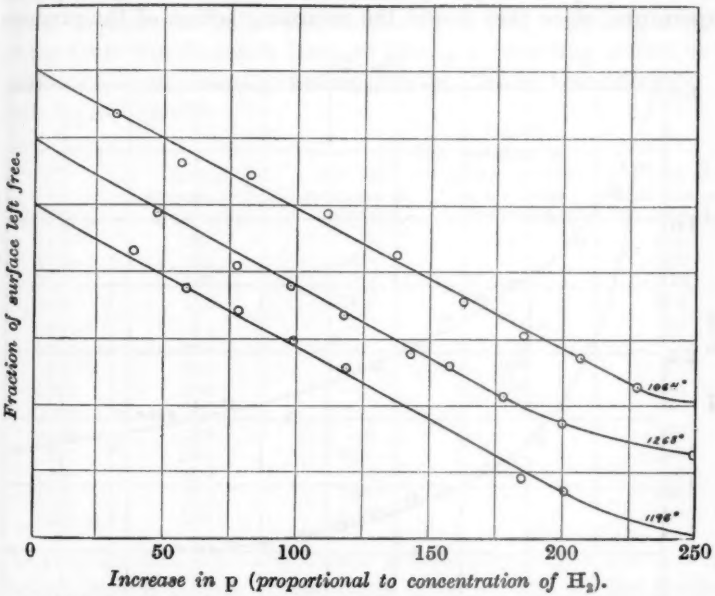
$$dx/dt = k[NH_3](1 - c[\text{products}])$$

or

$$dx/dt = k(a - x)(1 - cx).$$

It now remains to be seen whether, taking this equation as a first approximation, the value of n inferred from the influence of pressure on the time of half change needs modification.

FIG. 1.



The divisions of the vertical scale are 0·2 The three curves are each drawn from a different origin (taken as 1·0 in each case) to avoid superposition.

The integrated form of the above equation is

$$t = \frac{1}{k(1 - ca)} \log \frac{(1 - cx)a}{(a - x)}$$

and if $t = \tau$ when $x = a/2$

then

$$\tau = \frac{1}{k(1 - ca)} \log 2(1 - 1/2ac).$$

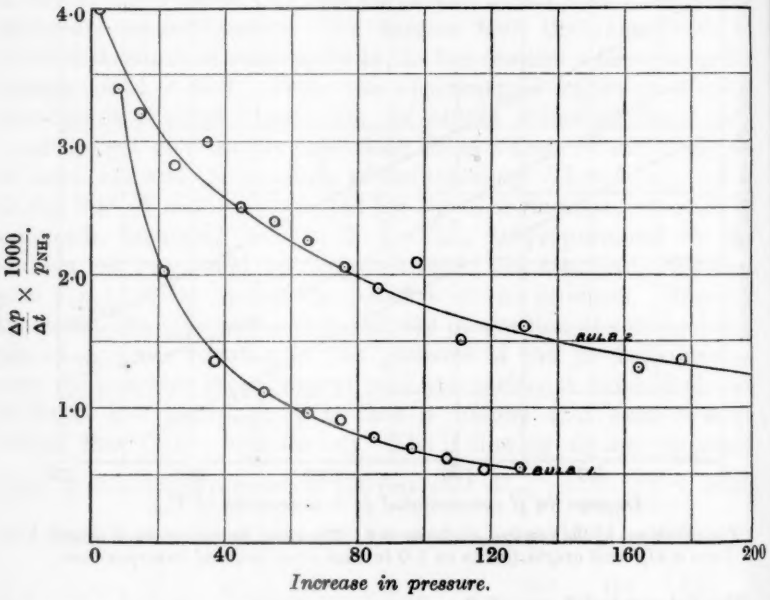
Putting $c = 0{\cdot}004$, we have, for $a_1 = 200$ mm., $\tau_1 = 0{\cdot}91/k$
and for $a_2 = 100$ mm., $\tau_2 = 0{\cdot}82/k$.

Thus the half life according to this equation should not remain quite steady when the pressure is reduced from 200 mm. to 100 mm., but should decrease by 10%. This, however, would not have been

enough to vitiate the conclusion that n is 1. The first approximation may therefore stand as sufficiently correct.

The relation between the pressure of the products and the amount of surface covered is not without interest. Up to 200 mm., which is not very far removed from the saturation limit, the adsorption isotherm of the reaction products is nearly linear, after which it bends sharply round and tends slowly towards saturation. The silica bulb used by Bodenstein and Kranendieck showed a quite different adsorptive capacity, and one which varied greatly with temperature, since they found the retarding action of the products

FIG. 2.



to be considerably greater at low temperatures than at high temperatures, whilst in the present experiments, the retarding influence is nearly independent of temperature.

At first, this difference in behaviour seemed rather surprising, but prolonged observation of one bulb through the course of seventy-five experiments, and the comparison of the two bulbs showed how remarkably variable the adsorptive capacity of the surface could be. Thus after bulb I had been used for about fifty experiments, including all those so far quoted, the character of its adsorption curve underwent a considerable change, assuming the form shown in Fig. 2. During two or three experiments the curves were of a transition type. This may have been associated with a

slow devitrification of the surface, but is probably due to a more subtle change in the configuration of the surface, since a completely new bulb also yielded adsorption curves of this form.

The great sensitiveness of the silica in regard to adsorptive capacity explains another striking difference between the present results and those of Bodenstein and Kranendieck. These observers state that while nitrogen and hydrogen together retard the reaction, nitrogen and hydrogen separately exert no retarding influence. This seems very remarkable and quite inexplicable, and repetition of the experiment failed to confirm the result. Hydrogen added to the bulb was found to have as strong a retarding action as the products of the reaction acting jointly. Thus the following are some typical results :

T (abs.).	Initial pressure of ammonia.	Initial pressure of hydrogen.	Initial pressure of products from a previous experiment.	Time of half change in seconds.
1196°	288	0	—	140
1194	302	200	—	515
1194	306	0	—	116
1195	222	200	—	304
1321	293	—	0	15
1323	290	—	0	13
1321	292	—	100	38
1321	298	—	200	31
1321	285	—	0	10
1226	278	0	—	90
1225	248	200	—	547
1226	280	0	—	61
1225	219	100	—	424
1225	201	200	—	844

The very marked retarding action of added hydrogen is sufficiently evident, and is clearly of the same order as that of the products of the reaction. The hydrogen was pure electrolytic hydrogen from a cylinder. The explanation of the discrepancy seems to be as follows. The mixture of nitrogen and hydrogen which Bodenstein and Kranendieck found to retard the reaction consisted of the reaction products left in from a previous experiment. These had been formed *in situ* on the surface, and under these conditions it would appear that the hydrogen remained adsorbed, whilst, when introduced from outside, it apparently did not readily attach itself to the surface. In view of the demonstrated sensitiveness of the silica surface, this seems quite possible, and indeed other examples of the phenomenon are known. Thus Freundlich (" Kapillarchemie," 2nd edition, p. 203) quotes some experiments of Zisch in which carbon monoxide actually produced by the decomposition of nickel carbonyl poisoned the surface of the nickel, whilst added carbon monoxide had no action. Fresh light came accidentally in

the course of the present series of experiments. Numerous fruitless efforts were made to obtain an exact relation between the amount of hydrogen added and the initial rate of reaction, but at this point the activity of the bulb, which had been fairly constant, began to vary too much to allow accurate results to be obtained. At last, the retarding effect of added hydrogen seemed to disappear altogether unless the added hydrogen was allowed to remain in the bulb for some time before the introduction of the ammonia. Bulb II showed the retarding effect of hydrogen as well as bulb I.

The Effect of Temperature.—Bodenstein and Kranendieck found the temperature coefficient of the reaction velocity to be very small, and to be different at different stages of the reaction. Thus between 780° and 880° the initial rate increased 1·3 times only. This ratio increased with the amount of decomposition products in the bulb, reaching a value of about 4·2.

With Bulb I the results found in the present investigation were in the sharpest contrast with this. The temperature coefficient was very high, and showed no systematic change over the course of the reaction. The following numbers illustrate the constancy:

		Time in seconds for the decomposition to reach					
		10%.	20%.	30%.	40%.	50%.	60%.
1161° (Abs.)		73	184	310	543	746	1220
1064 „		280	630	1134	1773	2640	3660
	Ratio	*3·9*	*3·4*	*3·7*	*3·3*	*3·6*	*3·0*
1263 „		—	8	16	29	50	84
1219 „		—	40	90	180	312	484
	Ratio		*5·0*	*5·6*	*6·1*	*6·2*	*6·8*

Numerous other pairs of experiments showed sometimes a slight rise and sometimes a slight fall in the ratio.

This is in keeping with the experiments described above on the constancy of the adsorption of the products at various temperatures. Taking, therefore, the time of half change as the typical measure of the reaction rate, the following table shows the effect of the temperature on the reaction in bulb I. The usual straight line is obtained on plotting the logarithm of the time of half change against the reciprocal of the absolute temperature.

T (abs.)	1268°	1195°	1135°	1114°	1092°
Average τ in seconds ...	9	128	943	2430	7656

The rate of reaction increases nearly fifty times between 1100° and 1200° Abs.

There is no question of a homogeneous reaction surpervening, for in a second bulb at an equal temperature the reaction proceeded

at only a fraction of the rate observed in bulb I. Two examples will suffice.

	Bulb I (1268°).	Bulb II (1261°).
Time of half change (secs.)	9	790

The remarkable difference between the temperature influence in these experiments and in those of Bodenstein and Kranendieck led to the repetition of some of the experiments in this second bulb. The temperature coefficient was now only 2·6 for 100 degrees over the range 1250° to 1400° Abs., being thus double that observed by Bodenstein and Kranendieck (1·3), but in most striking contrast with that found for bulb I.

Initial Variations in the Activity of the Silica Surface.—In the first experiments made with bulb I its activity showed a marked and steady increase, and then remained constant for a long time. The initial increase could not have been due to progressive devitrification or other spontaneous change of the surface, since the bulb had been heated at 1318° for many hours before the first experiment, and then the whole series of eight determinations was carried out rapidly in quite a short time. Nor could the increase in activity have been due to reduction of the silica, since allowing the bulb to stand in contact with air did not remove the activity. It was concluded that the progressive increase must have been due to changes in the configuration of the surface caused by the actual process of decomposing ammonia.

Comparison with the Results of Bodenstein and Kranendieck and General Conclusions.—The main differences between the results of the two investigations are :

(1) Bodenstein and Kranendieck found that added hydrogen had no retarding influence, whereas it is now shown that it can have just as large a retarding influence as the products of the reaction formed *in situ*. This difference is attributed to the sensitiveness of the hydrogen adsorption to the exact configuration of the silica surface.

(2) Bodenstein and Kranendieck found the temperature coefficient to be very low, whereas we now find that it may have a very large value, but again is very sensitive to the exact nature of the surface.

(3) Bodenstein and Kranendieck found the retarding influence of the products to vary with temperature, whereas we have found that it can be constant over a range of 200 degrees. We find, however, that the shape of the adsorption isotherm of the products may undergo changes after prolonged use of the bulb.

These differences are not fundamental contradictions, and one of the principal points which emerges from the present investigation

is the extreme sensitiveness of the surface both with regard to activity in decomposing ammonia, and to the adsorptive capacity for the products of the reaction. The adsorption equilibria must be extraordinarily delicately balanced in this case, and can be completely shifted by slight changes in the configuration of the surface. A single example will show how this might be accounted for. Suppose adsorbed ammonia molecules were held by two adjacent silica molecules. At a higher temperature, the distance between adjacent silica molecules might have increased owing to changes in the exact configuration of the surface to such an extent that ammonia molecules could now be adsorbed only with great difficulty. Thus the amount of ammonia in a position to react would have diminished and the naturally high temperature coefficient of the rate of chemical change of the ammonia actually adsorbed would be reduced to an observed temperature coefficient with a quite low value. Were, however, the silica molecules more closely packed to begin with, adsorption of the ammonia might occur just as readily at the higher temperature, and the normal "chemical" temperature coefficient would not be masked. The remarkable fact that hydrogen formed in the reaction may remain adsorbed under conditions where hydrogen added to the bulb is not adsorbed seems to show that ammonia is adsorbed on silica by means of its hydrogen atoms.

Thermal Decomposition of Ammonia on a Heated Platinum Wire.

The apparatus used was identical with that used by Hinshelwood and Prichard for the catalytic decomposition of nitrous oxide. The temperatures were obtained from the resistance of the heated platinum wire, the temperature–resistance curve of a piece of the same wire being separately determined by comparison with a direct reading thermo-couple over the range of temperature used in the experiments. The pyrometer itself was checked by taking the boiling point of zinc and the melting point of antimony. Pure dry ammonia was used. The high thermal conductivity of the hydrogen produced during the reaction renders it necessary to increase continuously the electrical energy supplied to the wire, in order to keep the temperature at its original value. The energy supplied was controlled by a delicately adjustable rheostat so that the resistance of the wire remained constant throughout the experiment.

Kinetics of the Reaction.—Hydrogen has a marked retarding effect on the reaction, the rate being approximately inversely proportional to the amount of hydrogen present. This is shown

by the following experiments carried out at 1138°, with 100 mm. initial pressure of ammonia in each case :

Pressure of hydrogen added (mm.)	50	75	100	150
Pressure (mm.) of NH_3 decomposed in 120 seconds	33	27	16	10

The reaction velocity seems to increase indefinitely as the pressure of hydrogen is reduced, as the following experiment shows :

Pressure of NH_3 200 mm. $T = 1138°$.

Time (secs.)	10	60	120	240	360	720
Pressure (mm.) of NH_3 decomposed	28	56	72	89	100	120

The rapid falling-off in the rate of reaction as hydrogen is formed is evident. It is also clear that the actual rate of reaction during the first fraction of a second must be very great. These and the previous results justify one in assuming that approximately

$$-d[NH_3]/dt = k[NH_3]^n/[H_2] = k(a-x)^n/x.$$

This is quite different from the sort of retardation caused by hydrogen on a silica surface; where the rate of reaction is not inversely as the hydrogen pressure, but decreases linearly as the hydrogen pressure increases.

Nitrogen has practically no influence on the rate of reaction. Thus in one experiment at 1090°, 38% of the ammonia decomposed in 120 seconds in the absence of nitrogen and 40% in the presence of an equal volume of nitrogen.

The value of n in the velocity equation may be found as follows. If n is 1 in the above equation, it is easily shown that the time taken for a given fraction of ammonia to decompose is directly proportional to the initial pressure. This is approximately true. Thus we have at 1138° :

Initial pressure of ammonia (mm.).	Time required for decomposition of 40%.	50%.	60%.
100	90	180	330
200	170	360	720
Ratio	*1·9*	*2·0*	*2·2*

At a lower temperature the ratio of the times required for 20% decomposition was 1·83 for 100 mm. and 200 mm.

Influence of Temperature.—Experiments were made with ammonia at 100 mm. pressure. Each time an equal volume of hydrogen was added, since it is impossible to find the initial rate of reaction in the absence of hydrogen. The time taken for 20% of the ammonia to decompose is taken as a measure of the rate of reaction.

T (abs.)	1488°	1478°	1456°	1411°	1385°	1365°	1331°	1304°
Time in seconds (t)	18	44	55	110	306	1680	2040	7560

The best straight line drawn through the $(1/T)$, $(\log t)$ points gives a value for the heat of activation of approximately 140,000 calories.

It may be shown that where specific changes with temperature in the activity of the catalyst itself are not an important factor the apparent heat of activation in a retarded catalytic action of this type is approximately given by

Observed heat of activation = True heat of activation − heat of adsorption of reactants + heat of adsorption of retarding products.

The unusually high value found in this reaction must be attributed largely to the influence of the last term.

Thermal Decomposition of Ammonia on the Surface of Tungsten.

The reaction vessel used for these experiments consisted of a 32-volt Osram lamp, to which were sealed capillary tubes leading to the Gaede pump, to the ammonia supply, and to a mercury manometer, the volume of all connexions being negligible compared with that of the bulb. A battery of accumulators supplied the electrical energy. From the resistance of the wire while heated, its temperature was calculated using the data of Langmuir (*Physical Rev.*, 1916, **7**, 159). The reaction bulb was kept in melting ice, the amount of decomposition being measured by the change in pressure measured at 0°.

The wire was remarkably constant in activity; decomposition of the ammonia took place at rather lower temperatures than on platinum or silica, and was uninfluenced by the presence of hydrogen. These points are shown in the following table:

	Mm. decomposed.		
Temperature 856°. Time (secs.).	100 mm. NH_3. No H_2.	100 mm. NH_3. 100 mm. H_2.	100 mm. NH_3. No H_2.
100	13·5	14	13
200	23·5	24·5	23
300	33·5	34·5	33·5
400	42·5	44	43
500	51	52·5	51·5
700	—	67	67
800	75	—	—
1000	87	—	—
1200	96	—	—
∞	100	—	—

The reaction is very nearly of zero order with respect to ammonia. The following table shows that when the absolute pressure of ammonia is increased fourfold, the absolute rate of reaction increases by about one-third only:

Temperature 856°. Time (secs.).	Millimetres decomposed. 200 mm. of NH_3.	50 mm. of NH_3.	Temperature 856°. Time (secs.).	Millimetres decomposed. 200 mm. of NH_3.	50 mm. of NH_3.
100	14	12	800	92	—
200	27	20	1000	112	—
300	38	28	1200	132	—
400	48·5	35	1400	149	—
500	59	—	1800	178	—
600	70	—	2000	187	—

The first experiment in the above table has two other points of interest. The progress of the reaction is much more nearly linear than monomolecular, for example, 70 mm. change in the first 600 seconds and 132 mm. in 1200 seconds. Moreover the portion of the curve representing the decomposition from 50% onwards coincides with the curve obtained with 100 mm. of ammonia. This is a satisfactory check on the adequacy of the method of temperature control, namely, working at constant resistance, since the electrical energy supplied in one case was nearly double that supplied in the other.

The effect of temperature was examined, and the results are summarised in the following table:

T (abs.).	Time (secs.) to reach 20% decomp. (t).	$\log_{10} t$.	$1/T \times 10^6$.
904°	14,300	4·155	1106
958	3,600	3·556	1044
1005	1,320	3·121	995
1068	425	2·628	936
1129	161	2·207	886

The curve obtained by plotting $\log t$ against $1/T$ is a very good straight line, the points lie on it closely enough to justify "point to point" calculation of the heat of activation from the formula

$$E = \frac{2{\cdot}303 \times 1{\cdot}98 \times \log_{10} t_1/t_2 \times T_1 T_2}{T_2 - T_1}.$$

Taking the values corresponding to 1129° as origin, the values of E calculated from the other four results are 37,900, 38,200, 38,800, 40,000. The average is 38,700 calories. This value is very much lower than that for platinum; this seems clearly to be connected with the absence of a retarding hydrogen film, the influence of which on the observed heat of activation was indicated in the last section.

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CLIV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XI. The Halogenation of Ethyl Acetylsuccinate.*

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In previous papers it has been established that the halogen atom in the α-position in 1 : 3-ketonic esters is reduced by hydrazine, and the reaction has now been applied to the study of halogenated acetylsuccinic esters. Ruhemann and Hemmy (J., 1897, **71**, 330) found that the ethyl bromoacetylsuccinate they obtained by bromination of the parent ester in chloroform solution decomposed on distillation with the formation of ethyl bromide and ethyl ω-carboxy-α-methyltetronate. They therefore assigned the γ-bromo-structure to the ester, and this inference is supported by the present work, which shows that the bromo-ester similarly prepared liberates little nitrogen from hydrazine hydrate. Further, Wolff and Junker (*Annalen*, 1913, **399**, 309) have shown that when ethyl diacetylsuccinate is brominated in chloroform solution it also gives rise to the γ-bromo-derivative, for on heating the dibromo-ester ethyl bromide and bistetronic acid are obtained.

In the previous halogenations of 1 : 3-diketones substitution occurred between the two carbonyl groups, and the α-halogenation of acetylsuccinic ester was therefore to be expected. Direct γ-halogenation would necessitate a prior enolisation involving the methyl group, and such a change is improbable (Auwers and Auffenberg, *Ber.*, 1917, **50**, 929). It is now clear, however, that the formation of the γ-bromo-derivatives must be accounted for by the migration of the halogen atom from the α-position where it first enters: cases of such migration are well established in the acetoacetic esters (Hantzsch, *Ber.*, 1894, **27**, 356, 3169; Conrad, *Ber.*, 1896, **29**, 1042).

By chlorination with sulphuryl chloride the α-chloro-derivative of ethyl acetylsuccinate is obtained, for the product is reduced almost quantitatively by hydrazine hydrate with the liberation of nitrogen and the formation of ethyl 3-methyl-5-pyrazolone-4-acetate by the action of excess hydrazine on the reduction product.

Phenylhydrazine reacts with this chloro-ester in an interesting way. Schonbrodt (*Annalen*, 1889, **253**, 197) investigated the action of this reagent on chloro-, bromo-, and iodo-acetoacetic esters, and isolated a derivative which Buchka and Sprague (*Ber.*, 1889, **22**, 2548) proved to be 4-benzenehydrazo-1-phenyl-3-methyl-5-pyrazolone. The reaction with α-chloroacetylsuccinate, however, cannot follow a similar course, the necessary α-hydrogen atom being

lacking. The product contains no chlorine, and gives no characteristic ketonic reactions. One molecule each of phenylhydrazine and of the chloro-ester are involved in the reaction, which produces *ethyl β-carbethoxy-γ-benzeneazo-Δ$^{\beta}$-pentenoate* (I):

$$\begin{aligned} &COMe{\cdot}CCl(CO_2Et){\cdot}CH_2{\cdot}CO_2Et \longrightarrow \\ &CMe(:N{\cdot}NHPh){\cdot}CCl(CO_2Et){\cdot}CH_2{\cdot}CO_2Et \longrightarrow \\ &CMe(N{:}NPh){:}C(CO_2Et){\cdot}CH_2{\cdot}CO_2Et \quad (I.) \end{aligned}$$

Support for this view is found in the formation of ethyl β-benzeneazocrotonate (II) from ethyl α-chloroacetoacetate and phenylhydrazine in ethereal solution (Bender, *Ber.*, 1887, **20**, 2747). On hydrolysis of the ester (I) an acid of the probable structure (III) is formed by loss of carbon dioxide.

(II.) $CMe(N{:}NPh){:}CH{\cdot}CO_2Et$ $\qquad$ $CMe(N{:}NPh){:}CH{\cdot}CH_2{\cdot}CO_2H$ (III.)

A good yield of the α-bromo-ester may be obtained if the bromination of ethyl acetylsuccinate is carried out in an aqueous solution of potassium hydroxide. Brominations previously carried out by introducing the halogen into an ester by means of a rapid current of air (Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 216; Macbeth, J., 1923, **123**, 1122) gave in all cases the α-bromo-derivative. When acetylsuccinic ester is thus brominated, the product contains only some 26% of the α-bromo-ester. Migration of the halogen atom from the α- to the γ-position therefore occurs much more readily in this than in the case of the acetoacetic esters, the trace of hydrogen bromide present being sufficient to induce the change; and therefore it is not surprising that the γ-bromo-ester is formed during bromination in chloroform, where the hydrogen bromide formed is mostly retained.

The behaviour of ethyl chloro- and bromo-nitromalonates is of some interest in connexion with polarity and other views. These compounds do not possess the hydrogen atom necessary to give the *aci*-form of the salts, and the tendency to acquire such an atom must be regarded as a potential factor in the reactivities of the compounds. Ethyl bromonitromalonate is vigorously reduced by hydrazine hydrate, with the liberation of the theoretical volume of nitrogen and the elimination of the halogen atom (Hirst and Macbeth, J., 1922, **121**, 911). In contrast with this, the chloro-ester reacts without the evolution of any gas, giving the hydrazide of ethyl chloronitroacetate. Alcoholic ammonia reacts in a similar way, giving the corresponding ammonium salt.

In the first case, it is evident that the polarity effect manifests itself, the strongly positive bromine being removed; in the second case, where the halogen is not so positive, the tautomeric hydrogen is acquired by the elimination of a carbethoxy-group, the reaction

following a course somewhat similar to the removal of a carbethoxy-group from ethyl nitro*iso*succinate by alcoholic ammonia with the formation of the ammonium salt of ethyl *aci*-nitropropionate (Steinkopf and Supan, *Ber.*, 1910, **43**, 3245).

Experimental.

Ethyl α-Chloroacetylsuccinate.—Ethyl acetylsuccinate, prepared by the addition of a slight excess of ethyl chloroacetate to dry ethyl sodioacetoacetate suspended in benzene, was obtained in good yield as an oil, b. p. 139°/12 mm.

Sulphuryl chloride (15 g.) was gradually added to 22 g. of the ester, hydrogen chloride and sulphur dioxide being briskly evolved, and the mixture was heated on a water-bath for ½ hour. From the well-washed, dried (with sodium sulphate) ethereal solution of the product, *ethyl α-chloroacetylsuccinate* was obtained as a colourless oil, b. p. 140—142°/12 mm., $n_D^{17°}$ 1·4420 (Found: Cl, 13·7. $C_{10}H_{15}O_5Cl$ requires Cl, 13·8%).

Five c.c. of a solution (2·505 g. of the chloro-ester in 25 c.c. of alcohol), on treatment with hydrazine hydrate (50% solution), liberated 22·5 c.c. N_2 at 12·5°/754 mm., indicating the presence of 95·7% of the α-chloro-ester. The product of another experiment (5 g. of the chloro-ester in 10 c.c. of alcohol, and 50% hydrazine hydrate in slight excess) separated, on cooling, in small, glistening crystals which, twice crystallised from water, gave ethyl 3-methyl-5-pyrazolone-4-acetate in fine, silvery laminæ which appear as rectangular tables under the microscope, m. p. 166° (compare Curtius, *J. pr. Chem.*, 1894, **50**, 508).

Ethyl β-Carbethoxy-γ-benzeneazo-Δ$^{\beta}$-pentenoate (I).—Reaction between 10 g. of the chloro-ester, dissolved in alcohol (10 g.), and an excess of phenylhydrazine was started by warming. The solution gradually became deep orange-red, considerable heat being developed, and slowly solidified. The crystalline mass was washed with dilute spirit and recrystallised several times from 90% alcohol, the *pentenoate* separating in fine, lemon-yellow, rectangular needles, m. p. 188°. The compound is unchanged by treatment with an excess of phenylhydrazine in boiling alcohol (Found: C, 63·2; H, 6·4; N, 9·5. $C_{16}H_{20}O_4N_2$ requires C, 63·2; H, 6·6; N, 9·2%).

The ester (I) (3 g.) was boiled for 2 hours with 100 c.c. of 8% alcoholic potassium hydroxide, water added, and the alcohol removed under reduced pressure. The voluminous, orange-red precipitate obtained on acidifying the solution with hydrochloric acid was well washed with water, and, being difficult to purify by recrystallisation, was dissolved in alkali and reprecipitated by acid. The product dried in a desiccator to an orange-yellow solid,

m. p. 164—165° (decomp.), which was apparently the acid (III) (Found: C, 64·0; H, 5·3; N, 13·5. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%).

Ethyl α-Bromoacetylsuccinate.—To a cooled solution of 21·6 g. of ethyl acetylsuccinate in 100 c.c. of *N*-aqueous potassium hydroxide, a solution of 16 g. of bromine in 150 c.c. of methyl alcohol was added until the colour of the bromine was no longer discharged. The mixture was diluted with water, and the precipitated oil dissolved in ether. The ethereal solution was washed with very dilute sodium thiosulphate solution, dried with sodium sulphate, evaporated, and the residual oil distilled under diminished pressure; the main fraction, b. p. 144—146°/10 mm., $n_D^{17°}$ 1·4600, was ethyl α-bromoacetylsuccinate. Five c.c. of a solution (2·95 g. of the bromo-ester in 25 c.c. of alcohol), on treatment with hydrazine, liberated 19 c.c. N_2 at 13°/758 mm., corresponding with 81% of the α-bromo-ester.

The bromo-compound reacted with phenylhydrazine, but none of the product obtained in the case of the chloro-ester could be isolated. Heat was developed and the reaction mixture darkened to a deep orange-red; reduction seemed to occur, for nitrogen was evolved. On cooling, the mixture solidified to a crystalline mass of phenylhydrazine hydrobromide. In one experiment, a small quantity of the phenylhydrazone of ethyl acetylsuccinate, m. p. 85°, was isolated (Ruhemann, *loc. cit.*).

Ethyl γ-Bromoacetylsuccinate.—(*a*) Approximately the calculated quantity of bromine was vaporised and drawn with air through 15 g. of ethyl acetylsuccinate, cooled in ice. The bromo-ester obtained was washed repeatedly with dilute sodium thiosulphate solution and with water, dissolved in ether, dried with sodium sulphate, and the solvent removed. The residual oil (2·95 g.) was dissolved in 25 c.c. of alcohol; 5 c.c. of this solution liberated 6·3 c.c. N_2 at 21°/751 mm., which corresponds with an α-bromo-ester content of 25·9%. The ester decomposes on distillation.

(*b*) Bromine (8 mols.) reacted readily with ethyl acetylsuccinate in chloroform solution. The product was purified as described under (*a*), and the solvent was removed under diminished pressure. The residue oxidised hydrazine only to a slight extent, and so consisted mainly of the γ-bromo-ester.

Ethyl Chloronitromalonate.—Chlorine was passed into an aqueous solution of potassium *aci*nitromalonic ester (Wahl, *Compt. rend.*, 1901, **132**, 1052). The ethereal solution of the oil which separated was washed and treated as described above, *ethyl chloronitromalonate*, b. p. 127°/8 mm., being obtained on distillation (Found: Cl, 14·6. $C_7H_{10}O_6NCl$ requires Cl, 14·8%).

Hydrazide of Ethyl Chloronitroacetate.—When 50% hydrazine hydrate was added to an alcoholic solution of ethyl chloronitromalonate, scarcely any gas was evolved, but the mixture became warm, and soon filled with a mass of light yellow crystals. On recrystallisation from absolute alcohol, the hydrazide was obtained as a white solid, m. p. 120°. Under the microscope it appears as stellate masses of lath-like crystals (Found: N, 21·2; Cl, 17·9; N_2H_4, 16·15. $C_4H_{10}O_4N_3Cl$ requires N, 21·4; Cl, 17·9; N_2H_4, 16·0%).

Ammonio-derivative of Ethyl Chloronitroacetate.—When alcoholic ammonia was added to ethyl chloronitromalonate, the mixture became yellow, and soon changed to a crystalline mass. The product crystallised from 90% spirit in colourless needles, m. p. 115° (Found: N, 15·4; NH_3, 9·0; Cl, 19·3. $C_4H_9O_4N_2Cl$ requires N, 15·1; NH_3, 9·2; Cl, 19·3%).

Dilute sulphuric acid was added to an aqueous solution of the ammonio-derivative; the resulting oil, isolated by means of ether, had b. p. 77—80°/8 mm. and n_D 1·4410. Ethyl chloronitromalonate has b. p. 77°/8 mm. and n_D 1·4412 (Macbeth and Traill, this vol., p. 895).

We wish to express to the Department of Scientific and Industrial Research our acknowledgment of a grant which enabled one of us to participate in the work.

THE UNIVERSITY, DURHAM.
THE UNIVERSITY, ST. ANDREWS. [*Received, March 11th*, 1925.]

CLV.—*The Freezing Points of Hydrofluoric Acid.*

By JOHN DAVID CECIL ANTHONY and LAWSON JOHN HUDLESTON.

In any case of equilibrium in solution, where the law of mass action is satisfied by the concentrations of the various ionic or molecular species, these concentrations must be proportional to the activities of the substances concerned or, better, equal to them, since the unit of activity for each substance may be arbitrarily defined. Hydrofluoric acid appears to offer such a case in solutions of exceptionally high concentration. Davies and Hudleston (J., 1924, **125**, 260) determined the composition of solutions of this acid by combining their measurements of the transference number with the conductivity data of Deussen (*Z. anorg. Chem.*, 1905, **44**, 312). Their results showed fairly good constancy for the expression $[HF_2']/[F'][HF]$ even up to twice (weight) normal solution, whilst the concentration of the undissociated hydrogen

fluoride was only about nine-tenths that stoicheiometrically present. Such a case offers an exceptionally favourable opportunity for comparison with the results of freezing-point determinations, from which the variation of activity of the hydrogen fluoride with changing concentration may be calculated directly, without recourse to any theory of dissociation.

In addition, it was desired to determine the activity of hydrogen fluoride in its aqueous solutions up to concentrations such that vapour pressure measurements are possible. The existing data of Paternò and Peratoner (*Atti R. Accad. Lincei*, 1890, **6**, 306, quoted from Abegg's "Handbuch") being rather scanty, the work described below was undertaken.

The method adopted was essentially similar to that of Adams (*J. Amer. Chem. Soc.*, 1915, **37**, 394). Two pure wax cylinders were almost filled with finely-crushed ice, water being added to one and solution to the other, the difference in temperature between them being measured by a thermo-element. Stirring was effected by means of inner wax cylinders with pierced bottoms, placed against the sides of the outer vessels and reaching from about 2 inches from the bottoms to within about the same distance of the tops of these. Closely fitting wax plungers, also pierced, could be moved up and down within the inner cylinders by means of heavily waxed copper rods. A disk of waxed lead foil above each plunger was free to slide up and down the central rod. This acted as a valve; on the down-stroke it readily lifted and allowed the solution to pass through the holes in the plunger, on the up-stroke it automatically closed these holes, so the liquid was continually drawn from the bottom and discharged again over the top. This stirring proved very efficient.

In the final form of the apparatus the outer wax cylinders were fitted with overlapping, water-tight wax lids, which carried vertical wax tubes for the plunger rod, the thermo-element, and for sampling. These lids were sealed into a metal case, a little larger than the wax cylinder, to make an air-jacket, and the whole was immersed, almost to the top of the tubes, in a bath kept at the temperature of the solution inside. The regulation of this, for the cylinder containing solution, was effected by means of a freezing mixture, water at room temperature being run in as required. The other cylinder required merely to be surrounded with crushed ice. With this arrangement, thermal equilibrium could be maintained for over an hour, but, just at the time this final form was evolved, the work had to be abandoned. The actual readings recorded were made with less efficient arrangements, only wax insulation being employed and the temperature of the outer bath being less

accurately regulated, and it is to this that the observed irregularities must be attributed. As there is no immediate prospect of repeating the work with the improved apparatus, and as it so happens that the curve is of such a form that the final results are not greatly vitiated, it seems worth while placing on record what has already been done.

The thermo-element, constructed similarly to that of Adams (*loc. cit.*), consisted of fifty copper-constantan junctions at each end, all being waxed. It was calibrated against a Beckmann thermometer in the same apparatus, the depressions being produced by potassium chloride. An ordinary cell potentiometer was adapted by using an auxiliary standard of about 0·05 volt (checked before and after each measurement) from a shunt in a high resistance circuit, and readings were made to 0·006° (0·003° for the very dilute solutions).

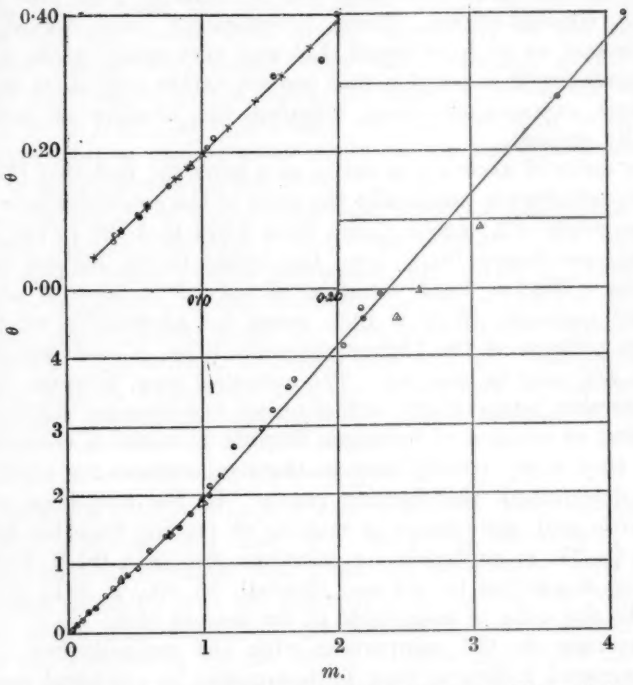
When equilibrium was established, a portion of the solution was withdrawn by means of a pure wax pipette and analysed by titration with sodium hydroxide, prepared by the method of Davies and Hudleston (*loc. cit.*) and standardised against benzoic acid.

The hydrofluoric acid for the dilute solutions was prepared as described by Davies and Hudleston (*loc. cit.*). The stronger solutions were prepared by treating potassium hydrogen fluoride with less than the theoretical amount of concentrated sulphuric acid in a platinum distilling flask. The side-tube of the flask was then sealed to a wax receiver, both being surrounded by ice-water, and the contents were distilled off from an oil-bath at 120°. The distillate contained more than 90% of hydrogen fluoride and was free from fluorosulphonic acid, since, after being diluted and boiled with bromine water, it gave no precipitate with barium chloride. Solutions were prepared from this by dilution, and the freezing points were consistent with those of solutions prepared by the other method.

The experimental results are recorded in Table I (where m is the molarity, mols. of hydrogen fluoride per thousand grams of water, and θ is the freezing point depression) and are shown graphically in the figures. Fig. 1 shows the whole range (with some of the data at low concentrations omitted for clarity), and in Fig. 1A the results in the more dilute solutions are shown on a larger scale. The general course of the curve is very nearly linear. This is of great assistance in tracing the best line through the somewhat discordant data; as a sinuous curve is highly improbable, the values at higher concentration check those at greater dilution. Thus the high points between M and $2M$-solutions cannot be reconciled with the remaining data without making the slope

first greater and then less, so their error is clearly indicated. The bend in the curve is sufficiently slight to be represented to a close approximation by a "smooth" curve composed of linear elements as drawn. This simplifies the calculation of activity changes, for if, for a given range of concentration, Δm, we have $\theta = Am + C$ (where A and C are constants), since $d \log_e a_2 = d\theta/\lambda m +$

FIG. 1A. FIG. 1.



⊙ *Experimental.* △ *Paternò and Peratoner.* × *Theoretical.*

$0{\cdot}00057\theta \,.\, d\theta/m$ (Lewis and Randall, "Thermodynamics," 1923, p. 286), this becomes

$$d \log_e a_2 = A \,.\, d \log_e m/\lambda + 0{\cdot}00057\theta \,.\, d\theta/m.$$

Changing to ordinary logarithms and noting that θ/m is sufficiently nearly 2 throughout, we get: $\Delta \log a_2 = A \,.\, \Delta \log m/\lambda + 0{\cdot}0005\Delta\theta$.

The data clearly cannot be extrapolated to zero on account of the dissociation of hydrofluoric acid, so it is necessary to define the activity arbitrarily for some one concentration. For reasons which will appear later, we have selected the value $a_2 = 0{\cdot}0876$ when $m = 0{\cdot}1$. Table II gives the result of the calculations for round molarities with the smoothed values of θ employed. It

might be emphasised that the activity coefficient, γ, given here is not the same as that usually employed for strong electrolytes, but is of the type used for non-electrolytes. Thus in dilute solution we should expect γm to be very nearly equal to the concentration of the undissociated hydrogen fluoride.

The values obtained by Paternò and Peratoner are also shown on the curves, marked as triangles. Their results agree closely with ours for dilute solutions, but are smaller than ours at the higher concentrations. These investigators used waxed glass vessels and, as we have found that wax very easily cracks at these temperatures, it is possible that contamination with silica occurred in their experiments, thus lowering the number of molecules actually present.

The order of accuracy is easily seen from the fact that the ratio of two activities is practically the ratio of the concentrations raised to the power A/λ, which varies from 1·023 to 1·196 in the curves as we have drawn them, from the lowest to the highest concentrations. With a total variation of only 7%, most of which is beyond question, there is little room for appreciable error and, except perhaps at the highest concentrations, a final accuracy of about 2% may be claimed. The activities may, however, have a considerable temperature coefficient for the stronger solutions, as the heat of solution of hydrogen fluoride in water is considerable. Thus they apply strictly only to the temperatures for which they were determined, the freezing points. In the analogous case of sulphuric acid, the change in activity on passing from the freezing point to 25° is negligible for solutions less than 0·1M and only 5% for M-solution (Lewis and Randall, *op. cit.*, p. 354), and this may be the order of magnitude in the present case.

Returning to the comparison with the concentration of the undissociated hydrogen fluoride determined by electrical measurements, we see, from the equation quoted above, that in dilute solution, if $a_2 = m$, $\theta = \lambda m$. Similarly, if a mixture of solutes be present to a total of n mols. per 1000 g. of water, and for each of them the activity is proportional to the molarity, then $\theta = \lambda n$.

On the assumptions previously used, we may calculate n for the case of hydrofluoric acid by solving (by successive approximation) the four equations (*a*) $[H^{\cdot}][F'] = K_1[HF]$, (*b*) $[HF_2'] = K_2[F'][HF]$, (*c*) $[H^{\cdot}] = [F'] + [HF_2']$, and (*d*) $m = [HF] + [F'] + 2[HF_2']$. No trustworthy data for K_1, and none at all for K_2, are known for 0°, but, as n is insensitive to their precise value, we have used the figures obtained by Davies and Hudleston at 25°, $K_1 = 7{\cdot}4 \times 10^{-4}$, $K_2 = 4{\cdot}7$, without fear of serious error. The values of λn resulting (shown as crosses on Fig. 1A) are entirely

compatible with the depressions determined experimentally for dilute solutions, definite divergence being hardly apparent before $m = 0{\cdot}5$. This in particular supports the postulate that no appreciable quantity of double molecules exists. Moreover, this result, taken in conjunction with the conductivity and transference number data, considerably strengthens the general theory. Thus any attempt to explain the slowly diminishing molecular conductivity at solutions above $0{\cdot}1M$ by the breakdown of the proportionality between active mass and concentration would almost certainly conflict with the results here given. According to the theory, the extra conductivity comes from the increasing quantity of complex ions, which do not affect the apparent molecular weight ($2HF = H^{\cdot} + HF_2'$), and [F′] does not increase with total concentration even as rapidly as it would do for a normal acid, and this is in accordance with the data.

The compositions of hydrofluoric acid solutions [calculated from equations (*a*)—(*d*)] at round molarities together with λn, the "theoretical" freezing-point depression, are given in Table III. It may be assumed with fair certainty that $a_2 = [HF]$ in at least the dilute solutions and hence we have selected the value 0·0876 at $m = 0{\cdot}1$. Below this, activities and activity coefficients are probably derived with more accuracy from these equations than by calculations from the freezing-point determinations.

Summary.

The freezing points of hydrofluoric acid have been determined for 0·025—$4M$-solutions, and the activities calculated. The postulate that hydrofluoric acid gives rise to complex ions, HF_2', in addition to simple ions has received confirmation, and the composition of the acid worked out on that assumption (together with that of the validity of the law of mass action applied to the concentrations) is supported. No appreciable amount of double molecules, H_2F_2, appears to exist.

TABLE I.

m	0·025	0·034	0·036	0·040	0·052	0·053	0·060	0·076
θ	0·056	0·069	0·078	0·085	0·108	0·107	0·123	0·150
m	0·082	0·100	0·104	0·109	0·154	0·190	0·201	0·259
θ	0·162	0·196	0·205	0·223	0·312	0·333	0·397	0·539
m	0·266	0·332	0·438	0·509	0·512	0·589	0·600	0·684
θ	0·494	0·642	0·840	0·948	0·954	1·104	1·182	1·320
m	0·694	0·719	0·758	0·812	0·819	0·849	0·865	0·901
θ	1·329	1·392	1·350	1·488	1·512	1·653	1·548	1·743
m	1·049	1·055	1·139	1·246	1·450	1·523	1·649	1·694
θ	1·986	2·117	2·250	2·697	2·958	3·219	3·567	3·648
m	2·056	2·187	2·203	2·331	3·649	4·140		
θ	4·131	4·692	4·553	4·895	7·783	8·990		

TABLE II.

m.	θ.	a_2.	$a_2/m=\gamma$.	m.	θ.	a_2.	$a_2/m=\gamma$.
0·10	0·196	[0·0876]	[0·876]	2·00	4·17	2·18	1·09
0·25	0·481	0·223	0·89	2·50	5·28	2·85	1·14
0·50	0·956	0·455	0·91	3·00	6·39	3·55	1·18
0·80	1·538	0·743	0·93	3·50	7·50	4·27	1·22
1·00	1·948	0·951	0·95	4·00	8·61	5·02	1·26
1·50	3·06	1·55	1·03				

TABLE III.

$m\times10$.	$[HF]\times10$.	$[F']\times10^3$.	$[HF_2']\times10^3$.	$[H^+]\times10^3$.	$[HF]/m$.	θ.
0·2	0·161	3·3	0·3	3·6	0·805	0·043
0·4	0·339	4·7	0·7	5·4	0·848	0·083
0·6	0·518	5·6	1·4	7·0	0·862	0·122
0·8	0·698	6·2	2·0	8·2	0·872	0·160
1·0	0·876	6·8	2·8	9·6	0·876	0·199
2·5	2·222	9·0	9·4	18·4	0·889	0·482
5·0	4·467	10·3	21·6	31·9	0·893	0·949
8·0	7·15	11·0	37·0	48·0	0·894	1·507
10·0	8·94	11·3	47·4	58·7	0·894	1·880

The calculated activities at the higher concentrations may be expected to have a considerable temperature coefficient.

In conclusion we wish to express our great appreciation of the kindness of the Scottish Oil Agency in providing special wax for this research.

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[*Received, February 10th*, 1925.]

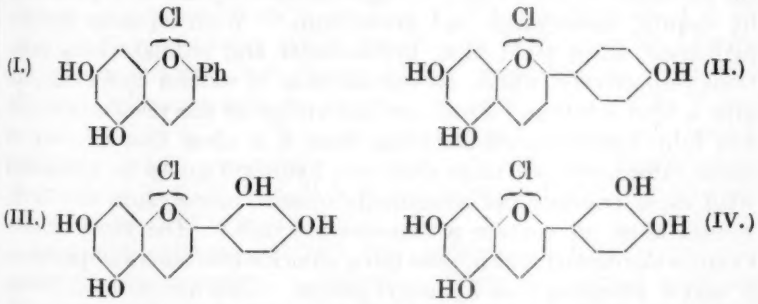
CLVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part VI. Polyhydroxyflavylium Salts related to Chrysin, Apigenin, Lotoflavin, Luteolin, Galangin, Fisetin, and Morin.*

By DAVID DOIG PRATT and ROBERT ROBINSON.

IN Part IV (J. 1924, 125, 200), we described methyl ethers of chrysinidin, apigeninidin and luteolinidin * and we now place on record a description of the corresponding phenols obtained on

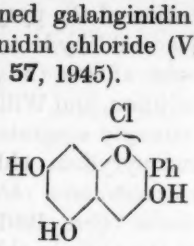
* In September, 1924, I had the privilege of a discussion with Professor Willstätter in the course of which he explained that, for example, the name "morinidin" is to be preferred to "moridin," because it leaves open the possibility of denoting an anthocyanin, which may be found in nature and which gives morinidin on hydrolysis, by the name "morinin." For the sake of uniformity, we accept this suggestion, and replace the admittedly more euphonious names, apigenidin, luteolidin, and galangidin by the expressions which appear in the text. Professor Willstätter also informed us that he and his colleagues had synthesised galanginidin and morinidin chlorides which we had obtained at that time by a different method.—R.R.

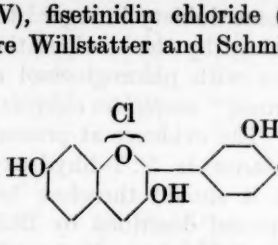
demethylation of the salts in the usual manner. At the moment there is some dubiety in regard to the constitution of the pyrylium salts obtained by the condensation of benzoylacetaldehyde and its derivatives with phloroglucinol and this doubt affects the compound termed "*acacetidin chloride*" (Pratt, Robinson, and Williams, *loc. cit.*). The evidence at present available strongly suggests that this substance is 5 : 7-dihydroxy-4-anisylbenzopyrylium chloride and that it should therefore be named *epiacacetinidin chloride*. The compound described by Bülow and Sicherer (*Ber.*, 1901, **34**, 3896) as 5 : 7-dihydroxy-2-phenylbenzopyranol (1 : 4) hydrochloride and obtained by the condensation of phloroglucinol and benzoylacetaldehyde should be identical with chrysinidin chloride, but it is in fact quite different from this substance. The method which depends on the condensation of a derivative of salicylaldehyde with a substance containing the group $-CO-CH_2-$ follows, however, an unambiguous course. Accordingly, we have adopted this process in order to obtain standard preparations of the flavylium salts of known constitution. 2-Hydroxy-4 : 6-dimethoxybenzaldehyde is condensed in presence of potassium hydroxide with acetophenone, 4-methoxyacetophenone, acetoveratrone, and 2 : 4-dimethoxyacetophenone to related chalkone derivatives, and these are all very readily converted by gently heating with mineral acids into pyrylium salts, from which chrysinidin (I), apigeninidin (II), lotoflavinidin (III), and luteolinidin (IV) chlorides are, respectively, obtained by demethylation with hydriodic acid followed by double decomposition of the iodides with silver chloride.



It is not necessary to adopt this indirect method in the case of ketones containing the group $-CO-CH_2\cdot OMe$. Galanginidin chloride trimethyl ether (Part III, J., 1924, **125**, 195) and fisetinidin chloride trimethyl ether (Part V, this vol., p. 170) have already been described. Morinidin chloride pentamethyl ether is similarly obtained by condensation of 2-hydroxy-4 : 6-dimethoxybenzaldehyde with ω : 2 : 4-trimethoxyacetophenone by means of hydrogen

chloride in ethereal solution. By the usual methods we have now obtained galanginidin chloride (V), fisetinidin chloride (VI) and morinidin chloride (VII) (compare Willstätter and Schmidt, *Ber.*, 1924, **57**, 1945).

(V.) 



(VI.)

The colour reactions of these salts are of interest. Only (IV) and (VI) give the intense ferric chloride reaction characteristic of cyanidin, which confirms the theory that the necessary condition for a positive result in the test is the occurrence of hydroxyl groups in the ortho-position to one another. (I), (II), (III) and (IV) do not exhibit the property of pseudo-base formation, whereas (V), (VI) and (VII) are readily decolorised in dilute solution. This confirms our earlier statement of the effect of a hydroxy-group in position 3 on ease of pseudo-base formation (Part III, p. 748).

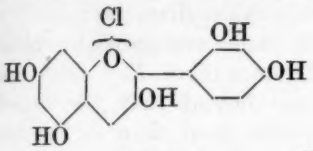
Fisetinidin (VI) closely resembles cyanidin in its behaviour with alkaline solutions and gives a pure blue coloration with aqueous sodium carbonate. On the other hand, luteolinidin (IV) gives a violet solution with sodium carbonate and this is changed to pure blue on the addition of sodium hydroxide. This behaviour throws some light on the constitution of certain anthocyanins. The researches of Willstätter and his co-workers have brought to light the existence of three types of diglucosides of cyanidin, represented by cyanin, mecocyanin and keracyanin.* With aqueous sodium carbonate, these yield blue, bluish-violet and reddish-violet solutions respectively, whilst, on the addition of sodium hydroxide, all give a blue solution. From our knowledge of the reactions of the less fully hydroxylated flavylium salts it is clear that in none of these substances can more than one hydroxyl group be combined with sugar residues and accordingly cyanin, mecocyanin and keracyanin must all contain a disaccharide unit.† The three anthocyanins mentioned give intense ferric chloride reactions and positions 3′ and 4′ therefore bear hydroxyl groups. This leaves the different colour reactions of cyanin, mecocyanin and keracyanin to be explained by the attachment of the carbohydrate to one of the positions 3, 5, and 7 in the cyanidin molecule and to a different

* Keracyanin is a rhamno-glucoside, but the nature of the sugars does not appear to affect the colour reactions in alkalis.

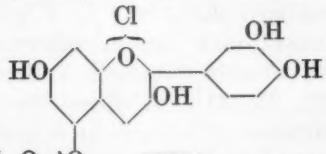
† This is probably true of the majority of the anthocyanins which are diglucosides and is confirmed by the identity of the reactions of mecocyanin and chrysanthemin, the monoglucoside obtained by partial hydrolysis.

position in each of the three cases. Now the effect of combining a phenolic hydroxyl with a residue of a disaccharide is doubtless greatly to reduce its auxochromic power and since cyanin so closely approaches cyanidin in its reactions it is evident that one of the hydroxyls at 3, 5, and 7 is of relatively small importance from the colour-producing point of view. The other two positions cannot be blocked without affecting the tinctorial power.

Fisetinidin and luteolinidin represent cyanidin with one hydroxyl group removed. The reactions of the former substance are scarcely distinguishable from those of cyanidin and this suggests that the unimportant hydroxyl is the one situated at position 5 and that cyanin chloride has the constitution (VIII). This is confirmed by



(VII.)



$(C_{12}H_{21}O_{10})O$ (VIII.)

the fact that luteolinidin shows the behaviour with alkalis characteristic of keracyanin and mecocyanin. The soundness of this argument depends on the correctness of the deduction that mecocyanin and keracyanin have free hydroxyl groups in different positions. If the reddish-violet and bluish-violet reactions described as characteristic of solutions of keracyanin and mecocyanin, respectively, in aqueous sodium carbonate represent an unimportant difference, then in each case the sugar residue may be attached to oxygen in position 3 or in position 7 (but not in position 5, 3′, or 4′). The expression (VIII) would then be a probable formula for cyanin chloride, but the possibility would remain open that the carbohydrate might be attached to oxygen in position 7 (but not in position 3, 3′, or 4′). In order to gain further information on this subject the preparation of a flavylium salt with free hydroxyls in positions 3, 5, 3′, and 4′ is being attempted, but the problem proves to be a difficult one.

Morinidin chloride exhibits two noteworthy peculiarities. It cannot be recovered by acidification of its decolorised solutions and the pseudo-base evidently undergoes some further transformation. On reduction by warming with zinc dust in dilute hydrochloric acid solution, it yields a colourless solution which exhibits only a slight tendency to become coloured in contact with air. Ether extracts from this solution a colourless substance which dissolves in dilute aqueous sodium hydroxide to a most intense and beautiful blue solution which becomes brownish-green and then yellowish-brown on heating. Cyanomaclurin, $C_{15}H_{12}O_6$, isolated

by Perkin and Cope (J., 1895, **67**, 937) from Jak-wood (from *Artocarpus integrifolia* Linn.) dissolves in aqueous sodium hydroxide to a colourless solution which becomes deep indigo, then green and brownish-yellow on heating. It is much more than a mere coincidence that A. G. Perkin (J., 1905, **87**, 715) assigned to cyanomaclurin a constitution which is that of a dihydromorinidin and we believe that the substance obtained by reduction of morinidin chloride is probably identical with an early transformation product of cyanomaclurin under the influence of alkali. It differs from the latter in giving at once the deep blue coloration with sodium hydroxide. By moderating the conditions of reduction we hope to achieve a synthesis of cyanomaclurin. Finally, it should be mentioned that 5 : 7 : 3′ : 4′-tetramethoxyflavylium bromide is not identical with the substance of the same composition obtained from catechin tetramethyl ether by Drumm (*Proc. Roy. Irish Acad.*, 1923, **36**, 41). A direct comparison showed that the catechin derivative is related to a much weaker base than is the tetramethyl-luteolinidin salt and there is no resemblance whatever between the two substances. We are indebted to Dr. Drumm for a specimen which has enabled us to make this comparison.

Experimental.

Chrysinidin Chloride (I).—The direct condensation previously employed for the preparation of dimethylchrysinidin salts (Part IV, J., 1924, **125**, 201) gives unsatisfactory yields, and it is preferable to isolate a chalkone derivative in the first place. Potassium hydroxide (8 g.) dissolved in water (12 c.c.) was added to a solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde * (6 g.) and acetophenone (4 g.) in methyl alcohol (25 c.c.), and the mixture maintained for 12 hours at 60°. The cooled, diluted, red liquid was acidified with acetic acid, and the precipitated viscous mass washed with water and stirred with a little ether. The bright yellow solid was collected, washed with ether, and dried (5 g.). *Phenyl 2-hydroxy-4 : 6-dimethoxystyryl ketone* crystallises from alcohol in pale yellow, rectangular plates, m. p. 136°. The substance is coloured deep red in contact with concentrated hydrochloric acid but, on heating, a clear orange solution is obtained from which dimethyl-

* The technique which we employ in applying the Gattermann synthesis of hydroxyaldehydes is described in Part III (*loc. cit.*, p. 195). The quantities are the following: Phloroglucinol dimethyl ether (17 g.); ether (150 c.c.); potassium cyanide (17 g.), the last decomposed by means of a mixture of concentrated sulphuric acid (17 c.c.) and water (17 c.c.). The washed product was hydrolysed at 80° for 15 minutes. Yield of crystallised material, 15 g. Or anhydrous phloroglucinol (21 g.), ether (300 c.c.), and potassium cyanide (23 g.) were employed and 20 g. of 2 : 4 : 6-trihydroxybenzaldehyde obtained.

chrysinidin chloride separates in orange-red needles. The corresponding *iodide* crystallises from an aqueous solution in red, microscopic needles. The dry chloride (2 g.) together with phenol (8 g.) was added to hydriodic acid (50 c.c.; *d* 1·7), and the mixture boiled in a neutral atmosphere for 20 minutes. The cooled liquid after addition of water and ether deposited chrysinidin iodide in bright red needles (1·8 g.), and after isolation the substance was converted, by means of silver chloride in dilute hydrochloric acid solution, into chloride, which crystallised from hot dilute hydrochloric acid in orange-yellow needles (Found: in material dried in a vacuum over sulphuric acid, C, 58·1; H, 5·0. $C_{15}H_{11}O_3Cl,2H_2O$ requires C, 58·1; H, 4·8%). This salt darkens at 130°, but does not melt at 300°. It is readily soluble in the simple alcohols to a red solution and in acetone to an orange-yellow solution. The yellow solution in concentrated sulphuric acid exhibits a weak green fluorescence. The colour base obtained by the action of sodium acetate on the salt is red and dissolves in aqueous sodium carbonate to a red solution the colour of which is neither intense nor persistent on dilution. The chloride dissolves moderately readily in warm water to a red solution which contains colour-base and becomes orange on the addition of a trace of hydrochloric acid. The *perchlorate* crystallises from acetic acid in long, orange-yellow needles which darken at 178° and melt at 185° (decomp.).

Apigeninidin Chloride (II).—5 : 7 : 4′-Trimethoxyflavylium chloride (3·4 g.) (Part IV, *loc. cit.*, p. 205) and phenol (10 g.) were added to hydriodic acid (80 c.c.; *d* 1·7) and the mixture boiled during 25 minutes in a neutral atmosphere. On cooling, the demethylated iodide separated to some extent in slender needles, but a further quantity crystallised on the addition of ether (3 vols.) to the liquid. The salt was isolated (2·2 g.) and converted to chloride by means of silver chloride in dilute aqueous hydrochloric acid solution. The orange, microscopic crystals were obtained by recrystallisation from alcohol in short, red needles which darkened at 180° but did not melt at 300° (Found: in material dried in a vacuum over sulphuric acid, C, 54·9; H, 4·8. $C_{15}H_{11}O_4Cl,2H_2O$ requires C, 55·1; H, 4·6%). A film of this salt deposited on glass has a fine green lustre. The orange-red solution in alcohol exhibits a weak green fluorescence on great dilution, whilst the fluorescence of the yellow solution in sulphuric acid is bright. The chloride is moderately readily soluble in water to a red solution containing colour-base, but is sparingly soluble in dilute hydrochloric acid and invariably crystallises from hot solutions in slender needles. The colour-base obtained by the action of sodium acetate has a port wine red colour and the salt or this base dissolves in aqueous sodium

carbonate or ammonia to a rich damson solution. In presence of sodium hydroxide, the ring is easily broken and on acidification of the orange-red solution with acetic acid a chalkone is precipitated. Mineral acids readily reconvert the latter into the pyrylium salt. The *perchlorate* crystallises from acetic acid in small, orange-yellow, rectangular prisms which darken at 190°, soften at 220°, and decompose at 222°.

5 : 7 : 2′ : 4′-*Tetramethoxyflavylium Ferrichloride*.—A mixture of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (4·5 g.), 2 : 4-dimethoxyacetophenone (4·5 g.), methyl alcohol (30 c.c.), potassium hydroxide (8 g.), and water (10 c.c.) was maintained at 60° for 8 hours. After dilution the chalkone was precipitated with acetic acid; the oil, washed with water, solidified in contact with methyl alcohol. The substance (3·5 g. when dry) crystallised from methyl alcohol in pale yellow, rectangular prisms, m. p. 154°.

2 : 4-*Dimethoxyphenyl* 2-*hydroxy*-4 : 6-*dimethoxystyryl ketone* is sparingly soluble in alcohol or ether, forms a red potassium salt, and on boiling with concentrated hydrochloric acid, best in presence of a little acetic acid, is rapidly and quantitatively converted into 5 : 7 : 2′ : 4′-*tetramethoxyflavylium chloride*, which is sparingly soluble in moderately concentrated hydrochloric acid and crystallises in red needles which decompose at 134°. The *ferrichloride* is sparingly soluble in hot acetic acid and crystallises in slender, red needles which decompose at 180° (Found: C, 43·6; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·5; H, 3·6%). The yellow solution in sulphuric acid exhibits green fluorescence and this is also characteristic of the orange-pink *iso*amyl-alcoholic extract of an acid aqueous solution. The solutions are decolorised by sodium carbonate or sodium acetate.

Lotoflavinidin Chloride (III).—A mixture of hydriodic acid (50 c.c.; *d* 1·7), phenol (5 g.), and 5 : 7 : 2′ : 4′-tetramethoxyflavylium chloride (2 g.) was boiled for 30 minutes in an atmosphere of carbon dioxide. The red needles which separated on cooling, together with a quantity obtained by addition of water and ether to the mother-liquor, were isolated (1·6 g.). The chloride was prepared in the usual manner, but in alcoholic solution, and separated on cooling in orange-yellow needles which darkened at 190° but did not melt at 300° (Found: in material dried in a vacuum over sulphuric acid, C, 52·8; H, 4·4. $C_{15}H_{11}O_5Cl,2H_2O$ requires C, 52·6; H, 4·4%). The yellow solutions in the simple alcohols and in sulphuric acid exhibit green fluorescence. The salt is sparingly soluble in cold dilute hydrochloric acid, but in the hot solvent yields an orange solution. The colour-base is deep red and the alkaline solution is reddish-violet. Except for the loss of blue tinge, little change occurs on heating with sodium hydroxide

because the sodium salt of the related unsaturated ketone appears to be deeply coloured. The reactions of lotoflavinidin are intermediate between those of apigeninidin and luteolinidin, but more nearly resemble those of the former.

Luteolinidin Chloride (IV).—5 : 7 : 3′ : 4′-Tetramethoxyflavylium chloride (Part IV, p. 206) (1 g.) was demethylated in the usual manner and, after the addition of much ether, luteolinidin iodide (0·6 g.) separated from the hydriodic acid solution in red needles. Conversion into the chloride was carried out in alcoholic solution containing a little hydrogen chloride by warming with silver chloride for 10 minutes. The salt separated from the hot solution in reddish-brown clusters of prisms and it was observed that the crystallisation was retarded by the presence of water (Found: in material dried in a vacuum over sulphuric acid, C, 52·8; H, 4·7; Cl, 10·1. $C_{15}H_{11}O_5Cl,2H_2O$ requires C, 52·6; H, 4·4; Cl, 10·4%). The salt darkens at 200°, but does not melt at 300°. The alcoholic solutions are red with a violet tinge and devoid of fluorescence; in sulphuric acid the yellow solution exhibits a faint green fluorescence. Luteolinidin chloride is more readily soluble in water and dilute hydrochloric acid than is lotoflavinidin chloride; the aqueous solutions are coloured magenta, bluish-violet, and pure blue by sodium acetate, sodium carbonate, and sodium hydroxide, respectively. The intense reaction with ferric chloride is violet-blue in alcoholic solution and reddish-violet in aqueous solution.

Galanginidin Chloride (V).—A mixture of 3 : 5 : 7-trimethoxyflavylium chloride (Part III, p. 195) (1 g.), phenol (2 g.), and hydriodic acid (25 c.c.; *d* 1·7) was boiled for 15 minutes in a neutral atmosphere. Difficulty was experienced in isolating the iodide and on one occasion ether was added and after some days crystals were observed and the process of separation was then assisted by the addition of light petroleum. Golden-brown platelets (0·4 g.) were collected (Found: in air-dried material, C, 32·1; H, 3·1. $C_{15}H_{11}O_4I,HI,3H_2O$ requires C, 32·0; H, 3·0%). This compound, apparently a di-iodide, has m. p. 145°. In other cases, the hydriodic acid mixture was diluted with water and ether, and the iodide (0·4 g.) obtained as a red powder. The related *chloride*, obtained in the usual manner, crystallised from dilute hydrochloric acid in red needles which darken at 160°, but do not melt at 300° (Found: in material dried in a vacuum over sulphuric acid, C, 55·0; H, 4·8. $C_{15}H_{11}O_4Cl,2H_2O$ requires C, 55·1; H, 4·6%). Willstätter and Schmidt (*loc. cit.*) have described a dihydrate of this salt, but this lost $1H_2O$ in a desiccator. Perhaps the exposure was longer or the vacuum higher. The colour of the solutions of the salt and its reactions agree with those described by Willstätter and Schmidt,

except that we find that the addition of sodium carbonate to the solid salt gives a port wine-coloured solution. The colour is transient, and not very persistent on dilution. The yellow solution in sulphuric acid exhibits green fluorescence.

Fisetinidin Chloride (VI).—7-Hydroxy-3 : 3′ : 4′-trimethoxyflavylium chloride (3·6 g.) (Part V, this vol., p. 170) was demethylated by a boiling mixture of phenol (8 g.) and hydriodic acid (90 c.c.; *d* 1·7) in 30 minutes. The iodide crystallised on cooling and a further quantity was precipitated by the addition of ether (2 vols.). The isolated product (2·2 g.) was dissolved in alcohol (40 c.c.) containing a trace of hydrogen chloride and treated at 60° for 10 minutes with an excess of precipitated silver chloride. Hydrochloric acid (25 c.c. of 7%) was added to the filtered solution, and the alcohol slowly removed by evaporation in a vacuum at the temperature of the room. Fisetinidin chloride crystallised in short, glistening, reddish-brown, prismatic needles with a violet sheen, and the process was repeated (Found: in material dried in a vacuum over sulphuric acid, C, 57·3; H, 3·9. $C_{15}H_{11}O_5Cl,0{\cdot}5H_2O$ requires C, 57·1; H, 3·8%). On heating, the salt gradually darkens but does not melt. In colour reactions, it closely resembles cyanidin, although the red solution in alcohol is perhaps a little more scarlet-red. The ease of formation of pseudo-base, the ferric chloride reaction, and the behaviour with sodium carbonate are identical with the corresponding properties of cyanidin chloride. Fisetinidin chloride reduces Fehling's solution in the cold and gives a bluish-violet precipitate on the addition of lead acetate to an alcoholic solution. The points of contrast with cyanidin are the following: (1) Fisetinidin chloride does not melt if immersed in a bath at 220°. (2) Solutions of the violet colour-base have a redder tinge than those of cyanidin colour-base. (3) The blue coloration given with ferric chloride in alcoholic solution fades more rapidly in the case of fisetinidin. (4) The yellow-orange solution of fisetinidin salts in sulphuric acid exhibits an apple-green fluorescence which becomes dark green on standing. The orange-red solutions of cyanidin salts in sulphuric acid exhibit at first no fluorescence and a weak green fluorescence on standing. (5) The blue alkaline solutions are more unstable in the case of fisetinidin than in the case of cyanidin.

3 : 5 : 7 : 2′ : 4′-*Pentamethoxyflavylium Salts*.—Hydrogen chloride was passed through a solution of ω : 2 : 4-trimethoxyacetophenone *

* This substance was obtained in improved yield in the following manner. Aqueous sodium hydroxide (40 c.c. of 20%) was added in one portion to a mixture of ω-methoxyresacetophenone (15 g.) and methyl sulphate (40 c.c.), which was then agitated but not cooled. Subsequently a further quantity

(2·5 g.) and 2-hydroxy-4 : 6-dimethoxybenzaldehyde (2·2 g.) in pure ether (30 c.c.) for 1·5 hours. Crystallisation from the crimson solution was induced by scratching, but only a small amount separated and the whole product was therefore diluted with water, the ether evaporated, and the mixture boiled and filtered. Clusters of red needles (1·2 g.) separated; a *ferrichloride* (0·5 g.) was obtained from the mother-liquor. The *chloride*, decomposing at 155°, crystallises readily from hot dilute hydrochloric acid in slender needles exhibiting a green reflex, but appearing red by transmitted light. The salt can be quantitatively recovered by addition of acid to decolorised solutions containing the pseudo-base. The *ferrichloride* crystallises from acetic acid in bright red needles which decompose at 194° (Found: C, 43·1; H, 4·0. $C_{20}H_{21}O_6Cl_4Fe$ requires C, 43·3; H, 3·8%). This derivative is readily soluble in the simple alcohols and also in chloroform to red solutions.

Morinidin Chloride (VII).—3 : 5 : 7 : 2′ : 4′-Pentamethoxyflavylium chloride (1·7 g.) was mixed with phenol (5 g.), added to hydriodic acid (40 c.c.; *d* 1·7), and the whole boiled for 20 minutes in a neutral atmosphere. Water and much light petroleum were added and the precipitated black powder (probably a periodide) was collected (1 g.). Conversion into chloride was accomplished by means of silver chloride and a little silver in 10% hydrochloric acid, and the solution was boiled for only 5 minutes and then filtered. Longer treatment is disadvantageous. The chloride separated in a flocculent mass of slender needles which darkened at 100° and did not melt at 300° (Found: in material dried in a vacuum over sulphuric acid, C, 50·0; H, 4·4. $C_{15}H_{11}O_6Cl,2H_2O$ requires C, 50·3; H, 4·2%). Willstätter and Schmidt (*loc. cit.*) observed the formation of this hydrate, but again they noticed loss of $1H_2O$ in a desiccator. The description of morinidin given by these authors is, however, applicable to the salt we have prepared, especially in regard to the comparisons instituted with pelargonidin and cyanidin chlorides. The solubility of the salt is also in agreement with the description of Willstätter and Schmidt. The yellow solution of morinidin chloride in sulphuric acid exhibits only a weak green fluorescence. We have noticed that the blue alkaline solutions of many anthocyanidins are dichroic, and even if blue in thin layers or when dilute the colour is bluish-violet to reddish-violet to red in thicker layers or in greater concentrations. This dichroism is especially characteristic of alkaline solutions of morin-

of aqueous sodium hydroxide (50 c.c. of 20%) was introduced in about 3 portions. The oil solidified on cooling and was collected (13 g.); it crystallised from methyl alcohol in long, silky needles, m. p. 61° (compare Slater and Stephen, J., 1920, 117, 313).

idin. The interesting behaviour of morinidin on reduction is mentioned in the introduction.

One of us (D. D. P.) desires to thank the Carnegie Trust for a Fellowship which has enabled him to take part in this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, March 6th*, 1925.]

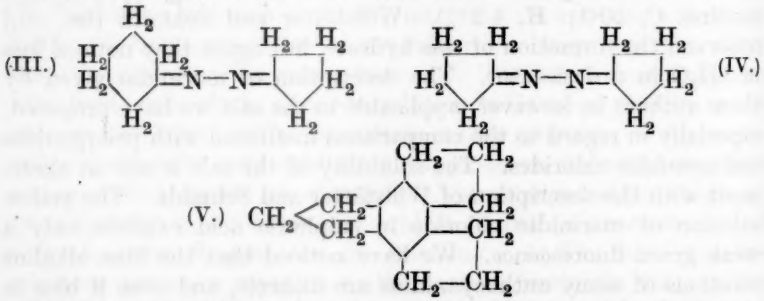
CLVII.—*The Action of Hydrogen Chloride on* cyclo*Hexylideneazine and on* cyclo*Pentylideneazine.*

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

A SHORT time since (J., 1924, **125**, 1503), we showed that *cyclo*hexylideneazine (I) is converted into octahydrocarbazole (II) when its solution in tetrahydronaphthalene is treated with hydrogen chloride at 180°.

(I.) (II.)

We have now investigated the action of hydrogen chloride under the same conditions on *cyclo*hexylidene*cyclo*pentylideneazine (III) and on *cyclo*pentylideneazine (IV), but in neither case has a pyrrole derivative corresponding to octahydrocarbazole (II) been obtained.



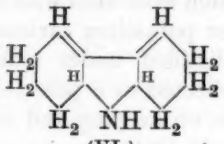
(III.) (IV.)

(V.)

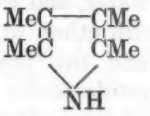
The decomposition of *cyclo*pentylideneazine with hydrogen chloride resulted in the formation of a hydrocarbon (m. p. 97°) of the empirical formula C_5H_6, and it was suggested to us by Prof. Robinson that this unexpected product of the removal of hydrazine from the azine might be tri*cyclo*trimethylenebenzene (V). Such proved to be the case, for the substance is identical with a specimen (m. p. 96—97°) of this hydrocarbon which we obtained by Wallach's method

(*Ber.*, 1897, **30**, 1094) from *cyclo*pentanone by treatment with hydrogen chloride.

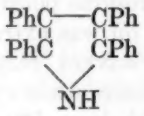
The formation of octahydrocarbazole from *cyclo*hexylideneazine is clearly a change exactly analogous to the conversion of phenylbenzylketazine into tetraphenylpyrrole (VIII) (Robinson and Robinson, J., 1918, **113**, 639), but the properties of the derivatives of our octahydrocarbazole are very different from those of the substances to which von Braun and Ritter (*Ber.*, 1922, **55**, 3792) have assigned identical structures. Quite recently (*Ber.*, 1925, **58**, 389) von Braun and Bayer suggested that our octahydrocarbazole has the structure represented by (VI) and they maintain that the fact that it can be easily methylated and ethylated and that the products yield methiodides is inconsistent with the behaviour of pyrrole derivatives. Quite apart from the difficulty of explaining the formation of structure (VI) from *cyclo*hexylideneazine by the removal of ammonia, we cannot agree with the arguments von Braun and Bayer bring forward against our view that formula (II) represents our octahydrocarbazole. It is well known that tetra-alkylated pyrroles exhibit properties which differ in many ways from those of pyrrole and its other derivatives. It is clear that formula (II) represents our octahydrocarbazole as being analogous in constitution to a tetra-alkylated pyrrole such as tetramethylpyrrole (VII) and we find that the two substances have in fact many properties in common.



(VI.)



(VII.)



(VIII.)

We have prepared tetramethylpyrrole and have confirmed the strongly basic character observed by Fischer and Bartholomäus (*Z. physiol. Chem.*, 1912, **80**, 6) and, although, owing to its instability in air, we have not been able to obtain a pure sample of the methyl derivative, there can be no doubt that tetramethylpyrrole reacts energetically with methyl iodide. The alkyl derivatives of our octahydrocarbazole are also unstable on exposure to air, but less so than the derivatives of tetramethylpyrrole appear to be. We consider, therefore, that the properties of our octahydrocarbazole are those which would be expected in a substance of structure (II) and until very definite evidence in support of such a view is forthcoming, it is clearly unjustifiable to assume that the removal of ammonia from *cyclo*hexylideneazine proceeds in a manner so abnormal as to give rise to a substance of constitution (VI).

The introduction of methyl groups into the nucleus of pyrrole evidently much enhances the basic nature of this substance and it seemed probable that the corresponding introduction of phenyl groups should have the opposite effect, that is to say, would confer acid properties on the >NH group. The examination of the properties of tetraphenylpyrrole (VIII) bears out this view, since this substance is insoluble in dilute acids, does not combine with methyl iodide, and crystallises unchanged from methyl sulphate. On the other hand, the acidic properties of the substance are evidenced by the fact that it yields a methyl derivative when it is treated with methyl sulphate in the presence of potassium hydroxide, obviously because of the intermediate formation of the *N*-potassium derivative (compare Fehrlin, *Ber.*, 1889, **22**, 555). It is interesting that this methyl derivative crystallises unchanged from methyl sulphate.

The action of hydrogen chloride on *cyclo*hexylidene*cyclo*pentylideneazine (III) was investigated under a variety of conditions, but in all cases resinous products were obtained from which nothing crystalline could be isolated.

Experimental.

cyclo*Pentylideneazine.*—*cyclo*Pentanone (45 g.), dissolved in alcohol (120 c.c.), was mixed with hydrazine hydrate (16 g.), the solution boiled on the steam-bath for 15 minutes and then allowed to stand for several hours. The alcohol was removed by distillation, the residue poured into water, and the solution saturated with salt. The oil was extracted with ether, dried over potassium carbonate, the solvent removed, and the product distilled under reduced pressure, when cyclo*pentylideneazine* was collected as a pale yellow liquid, b. p. 130—132°/22 mm. It solidifies on keeping and melts at 25° (Found : N, 17·0. $C_{10}H_{16}N_2$ requires N, 17·1%).

A solution of *cyclo*pentylideneazine (20 g.) in tetrahydronaphthalene (80 c.c.) was dropped gradually into a small quantity of dry tetrahydronaphthalene, maintained at 180°, through which a stream of dry hydrogen chloride was passed continuously. The solvent was removed in steam, the residue made alkaline with sodium carbonate, and the product extracted with ether. The solution was dried over potassium carbonate, the solvent removed, and the almost black residue was distilled under reduced pressure, when a small quantity of an oil, b. p. 180—185°/30 mm., was collected. This solidified, on cooling, and was recrystallised from alcohol, from which tri*cyclo*trimethylenebenzene separated in long, colourless needles, m. p. 97° (Found : C, 90·8; H, 9·1. Calc. for $C_{15}H_{18}$, C, 90·9; H, 9·1%). A specimen was prepared by the method described by Wallach (*loc. cit.*) and a mixture of the two melted at 97°.

1-*Methyltetraphenylpyrrole*.—Tetraphenylpyrrole (5 g.) was dissolved in acetone (50 c.c.) and treated with methyl sulphate (15 c.c.) and potassium hydroxide (30 g. in saturated aqueous solution) alternately in successive small quantities, during the course of an hour, with continuous shaking. The mixture was diluted with water and the product recrystallised from acetone, from which pure 1-*methyltetraphenylpyrrole* (3·1 g.) was obtained in colourless plates, m. p. 210° (Found: C, 90·5; H, 6·1. $C_{29}H_{23}N$ requires C, 90·4; H, 6·0%).

1-Methyltetraphenylpyrrole is insoluble in dilute acids and can be crystallised unchanged from hot methyl sulphate.

cyclo*Hexylidene*cyclo*pentylideneazine*.—Hydrazine hydrate (35 g.) was dissolved in alcohol (100 c.c.) and treated gradually with *cyclo*hexanone (50 g.) with continuous shaking. The mixture was boiled for 5 hours, the alcohol removed, and the residue distilled under reduced pressure. A fraction (11 g.), b. p. 105—110°/22 mm., was collected consisting of *cyclo*hexanonehydrazone (compare Mailhe, *Compt. rend.*, 1922, **174**, 465); the main product of the reaction being *cyclo*hexylideneazine, b. p. 153°/22 mm. A mixture of the *cyclo*hexanonehydrazone with *cyclo*pentanone (8·5 g.) was heated on the steam-bath for an hour, and the product dissolved in ether and dried with potassium carbonate. After removal of the solvent, a fraction was obtained, b. p. 140—145°/12 mm. This proved to be cyclo*hexylidene*cyclo*pentylideneazine*, but the yield was not good (Found: N, 15·5. $C_{11}H_{18}N_2$ requires N, 15·7%).

One of us (S.G.P.P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, March 31st*, 1925.]

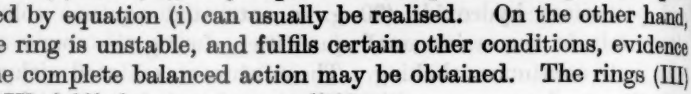
CLVIII.—*The Additive Formation of Four-membered Rings. Part VII. The Synthesis and Division of Some Dimethylene-*1 : 3*-oxaimines.*

By CHRISTOPHER KELK INGOLD.

ATTENTION has been directed in previous parts of this series to reversible additive ring formation involving a double equilibrium of the type

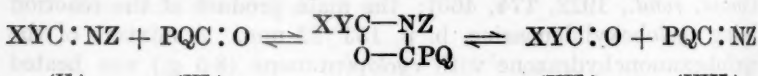
$$\begin{matrix} A & C \\ \| & \| \\ B & D \end{matrix} + \begin{matrix} \| \\ \| \end{matrix} \rightleftharpoons \begin{matrix} A{-}C \\ | \quad | \\ B{-}D \end{matrix} \rightleftharpoons \begin{matrix} A{=}C \\ + \\ B{=}D \end{matrix} \quad . \quad . \quad . \quad (i)$$

When the intermediate cycloid is stable, as in the case of the ring systems (I) and (II), only a part of the equilibrated system represented by equation (i) can usually be realised. On the other hand, if the ring is unstable, and fulfils certain other conditions, evidence of the complete balanced action may be obtained. The rings (III) and (IV) fulfil the necessary conditions:



Equilibria dependent on the formation and division of rings of type III were discussed in Part I (Ingold and Piggott, J., 1922, 121, 2793), and similar equilibria dependent on type IV are now described.

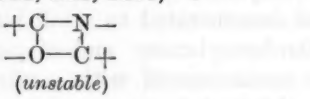
Rings of this type are produced from carbonyl compounds and azomethines, and their division in the two possible directions may give rise to double-bonded products of the same two classes:



This reaction can be determined completely in either direction in favour of an insoluble participant; thus, if (VIII) is insoluble in some solvent, such as ethyl acetate, it will, in a short time, be quantitatively deposited from an ethyl acetate solution of (V) and (VI), whilst the mother-liquor will yield (VII) on evaporation (see Section B). In a solvent, however, in which all the participants in the balanced action are readily soluble an equilibrium is attained which can be approached from either end (see Section A).

In some of the cases formerly examined (Part I, *loc. cit.*), the isolation of the extremely unstable intermediate cycloids (type III) was achieved, but in the present experiments cycloids of type (IV) could not be isolated, such rings being, on the whole, apparently even less stable than those of type (III). In connexion with this difference of stability it is of interest that the union of azomethines and carbimides, which might be expected to yield a ring either of type (III) or of type (IV), actually gives type (III) alone, moderately stable compounds of this class having been obtained by Senior and Shepherd (J., 1909, 95, 504) and by Hale and Lange (*J. Amer. Chem. Soc.*, 1919, 41, 384):

It is also noteworthy that the dimethylene-1 : 3-oxaimine rings (type IV), in which the polarities may be said to be concordant, are so unstable, whereas the "isomeric" dimethylene-1 : 2-oxaimine rings (type II), in which the polarities are discordant, or, at least, less concordant, are quite the most stable four-membered heterocyclic rings which have been produced up to the present time (Ingold and Weaver, J., 1924, **125**, 1456) * :



EXPERIMENTAL.

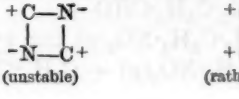
The aldehydes and azomethines produced in the reactions described in Section A were each identified by comparison and by the m. p. of a mixture with an authentic specimen.

(A) Additive Reactions between Carbonyl Compounds and Azomethines Leading to Equilibria which can be Approached from Both Sides.

(i) *The Reaction* : $(p)NO_2\cdot C_6H_4\cdot CHO$ + $(m)NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(p)$ $\rightleftharpoons$ cycloid $\rightleftharpoons$ $(p)NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(p)$ + $(m)NO_2\cdot C_6H_4\cdot CHO$.—

(a) *Formation of* p-*nitrobenzylidene*-p-*nitrobenzylamine and* m-*nitrobenzaldehyde from* p-*nitrobenzaldehyde and* m-*nitrobenzylidene*-p-*nitrobenzylamine.* Equimolecular quantities of *p*-nitrobenzaldehyde and *m*-nitrobenzylidene-*p*-nitrobenzylamine were mixed in solution in either ethyl acetate, chloroform or absolute alcohol. After some days, the solution was concentrated in a vacuum and seeded with p-*nitrobenzylidene*-p-*nitrobenzylamine*, with consequent deposition of a considerable quantity of this substance, which was crystallised from benzene and identified by analysis (Found : C, 58·9; H, 3·9. $C_{14}H_{11}O_4N_3$ requires C, 58·9; H, 3·9%) and by direct comparison with a specimen prepared from *p*-nitrobenzaldehyde and *p*-nitrobenzylamine. The mother-liquor was concentrated to a small bulk and the crystallisation of *p*-nitrobenzaldehyde and *m*-nitrobenzylidene-*p*-nitrobenzylamine induced by seeding. The ultimate residues were dissolved in 80% alcohol and extracted with successive quantities of benzene in the hope of isolating the cycloid. This was not obtained, but the earlier extracts yielded fairly pure *m*-nitrobenzaldehyde.

* A difference in the same sense, although less marked, exists between the dimethylene-1 : 2- and dimethylene-1 : 3-di-imines (this vol., p. 378) :



(b) *Formation of* p-*nitrobenzaldehyde and* m-*nitrobenzylidene*-p-*nitrobenzylamine from* p-*nitrobenzylidene*-p-*nitrobenzylamine and* m-*nitrobenzaldehyde.* Solutions of equimolecular quantities of *m*-nitrobenzaldehyde and *p*-nitrobenzylidene-*p*-nitrobenzylamine were mixed as before, and, after allowing time for equilibration, the solution was evaporated at a low temperature and the excess of *p*-nitrobenzylidene-*p*-nitrobenzylamine caused to crystallise and removed. The filtrate was concentrated to small bulk, and crops of *m*-nitrobenzylidene-*p*-nitrobenzylamine and of *p*-nitrobenzaldehyde, each more or less contaminated with *p*-nitrobenzylidene-*p*-nitrobenzylamine, were obtained by appropriate seeding. The aldehyde was purified by crystallisation from ethyl acetate, and the azomethine by many crystallisations from benzene. (For the azomethine : Found, C, 58·4; H, 4·1. Calc., C, 58·9; H, 3·9%).

(ii) *The Reaction :* (*p*) $NO_2 \cdot C_6H_4 \cdot CHO$ + (*m*)$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$(*m*) $\rightleftharpoons$ cycloid $\rightleftharpoons$ (*p*)$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$(*m*) + (*m*)$NO_2 \cdot C_6H_4 \cdot CHO$.—(a) *Formation of* m-*nitrobenzylidene*-m-*nitrobenzylamine and* p-*nitrobenzaldehyde from* p-*nitrobenzylidene*-m-*nitrobenzylamine and* m-*nitrobenzaldehyde.* This reaction was carried out like the last, and the *p*-nitrobenzaldehyde and *m*-nitrobenzylidene-*m*-nitrobenzylamine were caused to crystallise by seeding after the solution had been evaporated at a low temperature. Crystallisation of the aldehyde and of the azomethine was favoured by the addition of ethyl acetate and absolute alcohol, respectively, to the concentrated solution. The aldehyde was finally crystallised from ethyl acetate, and the *azomethine* from alcohol and then from benzene (Found : C, 58·7; H, 4·0. $C_{14}H_{11}O_4N_3$ requires C, 58·9; H, 3·9%).

(b) *Formation of* p-*nitrobenzylidene*-m-*nitrobenzylamine and* m-*nitrobenzaldehyde from* m-*nitrobenzylidene*-m-*nitrobenzylamine and* p-*nitrobenzaldehyde.* As much *p*-nitrobenzaldehyde and *m*-nitrobenzylidene-*m*-nitrobenzylamine as possible was crystallised from the equilibrated solution by cautious concentration in the cold, aided by seeding, and the residue was fractionally extracted by the benzene and aqueous alcohol process described above. From the earlier benzene extracts *m*-nitrobenzaldehyde was readily isolated, and from the later ones a mixture of azomethines, etc., from which *p*-nitrobenzylidene-*m*-nitrobenzylamine was obtained by alternate crystallisation from alcohol and benzene.

(B) *Reactions Determined in Favour of an Insoluble Participant.*

(i) *The Reaction :* (*p*)$NO_2 \cdot C_6H_4 \cdot CHO$ + $C_6H_5 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$(*p*) $\rightleftharpoons$ cycloid $\rightleftharpoons$ (*p*)$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$(*p*) + $C_6H_5 \cdot CHO$.—This reaction

went practically completely from left to right when *p*-nitrobenzaldehyde (1·5 g.) and benzylidene-*p*-nitrobenzylamine (2·4 g.) were dissolved in 5 c.c. of absolute ethyl alcohol. After some hours a crystal of *p*-nitrobenzylidene-*p*-nitrobenzylamine was introduced and the mixture kept until deposition of this substance ceased. The liquid was then evaporated to 2 c.c. with the aid of the pump and diluted with 5 c.c. of dry ether; crystals of nearly pure *p*-nitrobenzylidene-*p*-nitrobenzylamine were obtained in almost quantitative yield after 1 hour.

The ethereal mother-liquors were evaporated and the liquid residue was treated with an excess of aqueous semicarbazide acetate, when a nearly quantitative yield of benzaldehydesemicarbazone (m. p. 224°, and not 214° as stated in the literature) was obtained. Its identity was confirmed by hydrolysis and subsequent oxidation of the benzaldehyde to benzoic acid.

(ii) *The Reaction :* $(m)NO_2\cdot C_6H_4\cdot CHO +$
$C_6H_5\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(p) \rightleftharpoons$ cycloid $\rightleftharpoons$
$(m)NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(p) + C_6H_5\cdot CHO$. — *m*-Nitrobenzaldehyde and benzylidene-*p*-nitrobenzylamine were allowed to interact as in the last experiment, but in more concentrated solution. The yield of fully purified *m*-nitrobenzylidene-*p*-nitrobenzylamine was 80%. Benzaldehyde was isolated from the mother-liquor in the form of its semicarbazone in 90% yield. The products were identified as in the preceding experiment.

(iii) *The Reaction :* $(p)NO_2\cdot C_6H_4\cdot CHO +$
$C_6H_5\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(m) \rightleftharpoons$ cycloid $\rightleftharpoons$
$(p)NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(m) + C_6H_5\cdot CHO$.—This reaction was carried out like the preceding one, but after crystallisation of the *p*-nitrobenzylidene-*m*-nitrobenzylamine appeared to have ceased the conversion was rendered quantitative by slow evaporation at the ordinary temperature. The azomethine was isolated and identified like the isomerides previously mentioned, and the benzaldehyde as its semicarbazone, both being obtained in almost theoretical yield.

(iv) *The Reaction :* $(m)NO_2\cdot C_6H_4\cdot CHO +$
$C_6H_5\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(m) \rightleftharpoons$ cycloid $\rightleftharpoons$
$(m)NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_4\cdot NO_2(m) + C_6H_5\cdot CHO$.—This reaction was carried out exactly like the preceding one, and the products, benzaldehyde and *m*-nitrobenzylidene-*m*-nitrobenzylamine, both obtained in nearly quantitative yield, were isolated and identified in the same way.

Part of the expense of this work has been defrayed by a grant from the Chemical Society, to whom the author's thanks are due.

THE UNIVERSITY, LEEDS. [*Received, March 19th*, 1925.]

CLIX.—*The Explosion of Ammonia with Carbon Monoxide and Oxygen.*

By JOHN WILLIAM BEESON and JAMES RIDDICK PARTINGTON.

IN the experiments of Partington and Prince (J., 1924, **125**, 2018) on the explosion of ammonia with electrolytic gas ($2H_2 + O_2$) the extent of decomposition was found to increase with the proportion of electrolytic gas in the mixture. It was suggested that it would be of interest to repeat the experiments with a mixture of carbon monoxide and oxygen instead of electrolytic gas, since this contains no constituent common to the exploding mixture and the ammonia which is decomposed by the energy liberated in the reaction.

It has now been found that the decomposition of ammonia is, within the limits of experimental error, the same whatever the ammonia content of the combustible mixtures; the mean decomposition, when the initial mixture was at 380 mm. pressure and the steam produced was kept gaseous during the explosion, was 95·3%. The results are, therefore, quite different from those obtained with electrolytic gas. With certain mixtures of high ammonia content, explosion did not occur with a single spark, but ensued when a series of sparks passed through the mixture. Mixtures rather richer in ammonia could not be ignited even after prolonged sparking.

EXPERIMENTAL.

Pure ammonia and oxygen gases were prepared as in the previous research. The carbon monoxide was prepared by dropping cold concentrated sulphuric acid on sodium formate, washed with caustic potash solution, and dried over stick caustic soda and purified phosphorus pentoxide. All the gases were rigorously tested for purity.

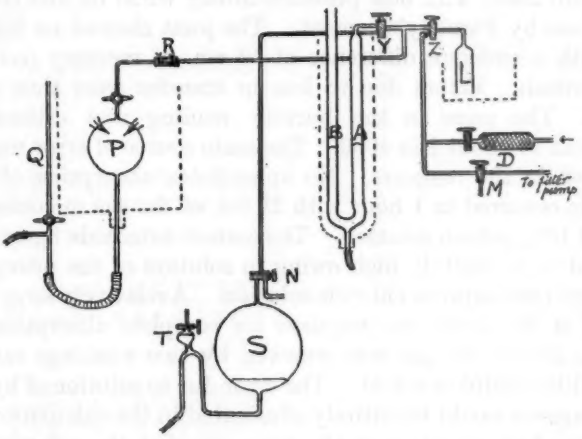
The apparatus used was carefully cleaned and dried after each experiment. The gases were collected by the displacement of dry mercury from the vessel L (Fig. 1), from which they could be transferred either to the measuring burette, A, or to the explosion pipette, P. A volume of 300 c.c. of the mixture $2CO + O_2$ was prepared and stored in the bulb S. The constituents of this mixture could be rapidly and completely absorbed by ammoniacal cuprous chloride solution and alkaline sodium hyposulphite solution.

The explosion pipette, P, was immersed in a copper bath, the water at first being at room temperature. In order to eliminate as far as possible the slight barometric and temperature changes during the mixing, the gases were measured out in the pipette in the order: 1 pipette CO; 1 pipette O_2; 1 pipette CO. After the explosion of 50 c.c. of the mixture, and absorption in potash, only about 0·03 c.c.

of unabsorbed gas remained. The gases were then transferred to the storage bulb, S, protected by the trap, T, and thoroughly mixed. When required, the gas could be forced into the vessel L and thence into the calibrated burette, A, for measurement. All readings were taken after an upward displacement of the mercury.

The *ammonia* gas, generated from pure materials (Partington and Prince, *loc. cit.*), was introduced through L; the part remaining in L was completely absorbed by dilute sulphuric acid. The mixture of ammonia, carbon monoxide and oxygen was then transferred to the bulb P, thoroughly mixed by splashing the mercury in the bulb, and heated to 85° in the water-bath. The volume was such that the bulb was just filled to the mark at a pressure of 380 $\pm$ 1 mm. at 85°. The gas was then fired.

FIG. 1.



The explosion in the case of mixtures having a low ammonia content was apparently instantaneous, the flame being blue. Mixtures containing 40·5% or more of ammonia did not fire at the first spark, but only after the mixture had been sparked from 1 second in the case of a mixture of 40·9% of ammonia to 4 or 6 seconds in the case of a mixture containing 46%. When the reaction occurred after this period of induction, the speed of propagation of the flame from the spark to the walls of the bulb was so slow that it could be followed by the eye.

The gas after the explosion was immediately passed back to the burette. As it cooled, water was deposited, carrying with it undecomposed ammonia and the carbon dioxide produced in the explosion. It was not possible, therefore, to measure the true volume of the total gaseous products of reaction. Attempts to liberate the carbon

dioxide by dilute acid were not successful, since the gas formed a highly supersaturated solution. The carbon dioxide was estimated from the difference between the carbon monoxide introduced and that found in the residue, after the carbon dioxide in the gas had been removed by washing with dilute potash solution. Potash (50%) absorbed carbon monoxide to an appreciable extent. The mixture of carbon monoxide, nitrogen and hydrogen was measured over boiled, dilute sulphuric acid (1 : 5), as were all the remaining volumes. The carbon monoxide was then absorbed by three washings of 4 c.c. of ammoniacal cuprous chloride solution. The residue of nitrogen and hydrogen was mixed with a large measured excess of oxygen and exploded in the bulb P. From the results the composition of the gaseous mixture after explosion could be calculated.

The only rubber connexions were the two shown in the figure. These were made with new pressure tubing wired on and cemented to the glass by Faraday's cement. The joint showed no leak overnight with a pressure difference of 50 cm. of mercury (cementing was essential). Errors due to loss in transfer were thus entirely avoided. The error in the burette reading was estimated by experiment at about 1 in 4000. The main source of error was in the absorption in the reagents. No appreciable absorption of carbon monoxide occurred in 1 hour with 23 c.c. of the gas in contact with 10 c.c. of 10% potash solution. The carbon monoxide figures would thus tend to be slightly high owing to solution of the nitrogen and hydrogen in the cuprous chloride solution. A relatively large volume (12 c.c.) of the latter was required for complete absorption. The ammonia left in the gas was removed by two washings each with 4 c.c. of dilute sulphuric acid. The error due to solution of hydrogen in the reagents would be entirely eliminated in the calculation of the percentage decomposition of the ammonia, but the solution of the nitrogen is a possible source of slight error. On the whole, the individual values of gas concentrations in the exploded mixture can probably be relied upon to about 1%. The values of the gas concentrations before explosion are probably accurate to well within 0·5%.

The results of the experiments are given in Table I. In experiments 8 and 15 periods of induction were observed. The volumes of carbon monoxide and hydrogen were directly determined in the exploded mixture. The volumes of the remaining constituents were calculated.

In Table II the relative volumes of the products of explosion in the mixture are calculated, together with the values of

$$K = [CO][H_2O]/[CO_2][H_2],$$

the constant of the water-gas equilibrium. A comparison of the

TABLE I.

TABLE I.

No. of Expt.	Composition of original gas. % NH_3.	% CO.	% O_2.	Volumes of products of explosion in c.c. CO.	H_2.	CO_2.	N_2.	H_2O.	NH_3.	Total.	% NH_3 decomp.
14	27·61	48·25	24·13	9·27	5·00	7·99	4·76	9·27	0·35	36·64	96·4
13	28·21	47·86	23·93	9·95	4·22	7·04	4·74	9·95	0·54	36·44	94·61
10	30·16	46·56	23·24	9·96	5·31	6·54	5·09	9·96	0·51	37·37	95·26
17	33·61	44·17	22·08	9·23	6·90	5·34	5·37	9·23	0·40	36·47	96·4
11	34·92	43·40	21·69	10·52	6·80	4·42	5·77	10·52	0·48	38·51	96·0
12	37·67	41·54	20·77	10·39	8·12	3·82	6·17	10·39	0·55	39·44	95·7
19	37·6	41·6	20·8	10·19	8·17	4·25	6·12	10·19	0·84	39·76	93·6
7	40·04	39·97	19·99	10·28	10·40	4·19	6·88	10·28	0·73	42·76	95·0
5	40·20	39·85	19·95	10·64	9·72	3·68	6·81	10·64	0·82	42·31	94·3
15	40·88	39·41	19·70	10·40	9·89	4·08	6·76	10·40	1·52	43·05	89·9
8	45·74	36·16	18·08	9·97	9·69	3·49	6·33	9·97	4·43	43·88	74·3
9	48·03	34·70	17·36	Gas could not be exploded even on prolonged sparking.							
18	49·33	33·78	16·89	,,	,,	,,	,,	,,	,,		

TABLE II.

Relative Volumes of Products of Explosion.

= Vols./total vol. of mixture.

$$K = \frac{[CO][H_2O]}{[CO_2][H_2]}.$$

Expt.	CO.	H_2.	CO_2.	N_2.	H_2O.	NH_3.	K
14	0·253	0·137	0·218	0·130	0·253	0·00957	2·14
13	0·274	0·116	0·193	0·130	0·274	0·0147	3·35
10	0·266	0·142	0·175	0·136	0·266	0·0136	2·85
17	0·253	0·189	0·146	0·147	0·253	0·0109	2·31
11	0·274	0·177	0·115	0·150	0·274	0·0125	3·69
12	0·261	0·206	0·097	0·157	0·261	0·0139	3·41
19	0·256	0·205	0·107	0·154	0·256	0·021	2·99
7	0·240	0·243	0·098	0·160	0·240	0·0170	2·42
5	0·251	0·230	0·087	0·161	0·251	0·0194	3·16

latter with the known values of the constant (Partington and Shilling, *J. Soc. Chem. Ind.*, 1925, **44**, 149T) shows that a water-gas equilibrium is set up as the gases cool after the explosion, the average temperature at which the equilibrium becomes fixed being in the neighbourhood of 1282° C. Calculation shows, as would be expected, that the ammonia equilibrium is not established.

Summary.

1. Mixtures of ammonia gas with $2CO + O_2$ in varying proportions were exploded at an initial temperature of 85° and pressure of 380 mm., so that no steam condensed during the explosion.

2. Mixtures containing more ammonia than corresponds with the ratio $NH_3/(2CO + O_2) = 0{\cdot}924$ could not be ignited by sparks. All mixtures which could be ignited showed approximately the same decomposition of the ammonia, *viz.*, 95·3%. With some mixtures richer in ammonia than 40·5% a period of induction was observed.

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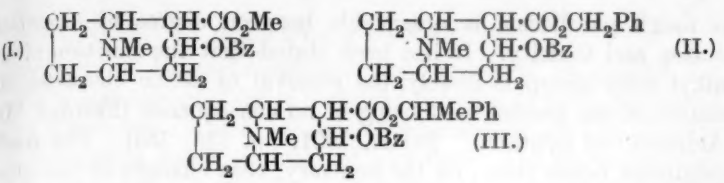
CLX.—*Aromatic Esters of Acylecgonines.*

By WILLIAM HERBERT GRAY.

NATURALLY-OCCURRING cocaine has served in several ways as a starting point in the search for the ideal local anæsthetic of low toxicity. The characteristics of its structure essential to the development of pronounced anæsthetic action are now recognised to be the amino- and acylated alcohol groups (I). A large variety of aminoalkyl esters, not containing the bridged ring of cocaine, has been synthesised and some of these, including "novocaine," "stovaine," and "β-eucaine," are in common use. In them, however, the power of penetrating mucous membrane possessed by cocaine, which, for example, renders it so valuable in causing corneal anæsthesia, is but feebly developed.

In another scheme, the tropane skeleton has been retained and the effect of variation of the ester groups investigated. Substitution of any other acyl radical for the benzoyl group very greatly diminishes the anæsthetic action, but the *O*-methyl group may give place to higher aliphatic homologues, yielding substances with the typical properties of cocaine (Merck, *Ber.*, 1885, **18**, 2954; Novy, *Amer. Chem. J.*, 1888, **10**, 147):



(I.) (II.)

(III.)

It seemed to be of particular interest to replace this methyl group by aromatic alcohol residues, aliphatic groups alone having been hitherto used. The simple aromatic alcohols have been shown to act as local anæsthetics (Macht, *J. Pharmacol.*, 1918, **12**, 263; Hirschfelder, Lundholm, and Norrgard, *ibid.*, 1920, **15**, 261). *Benzoyl*-l-*ecgonine* esters of *benzyl* (II), p-*nitrobenzyl*, o-*hydroxybenzyl*, α-*phenylethyl*, β-*phenylethyl*, and γ-*phenyl*-n-*propyl alcohols*, together with the *benzyl* and β-*phenylethyl* esters of *benzoyl*-d-ψ-*ecgonine*, have now been prepared, and, with the benzyl group in this position, the corresponding *tropoyl*, *salicyloyl*, and *hydroxytoluoyl* esters of *benzyl*-l-*ecgonine*. It was not found possible to esterify ecgonine with benzyl alcohol by the ordinary Fischer-Speier procedure, nor to effect an interchange of ester groups by heating cocaine with benzyl alcohol. Treatment of the sodium salt of benzoylecgonine with the appropriate aralkyl chloride was, however, found to give the desired esters in good yield. With two exceptions, these were obtained as oils at the ordinary temperature; their picrates, but not the other salts, also have unusually low melting points. The salts of the *d*-ψ-ecgonine derivatives show the comparatively sparing solubility in water which characterises *d*-ψ-ecgonine derivatives in general. Attempts to prepare the simplest representative, phenylbenzoyl-*l*-ecgonine, were unsuccessful.

The anæsthetic and toxic effects of these substances have been studied by Dr. J. Trevan and Miss E. M. Boock, of the Wellcome Physiological Research Laboratories, to whom the author desires to tender his warmest thanks. Their results are here briefly summarised and will be published in full at a later date. All the new esters, with three exceptions, are more active anæsthetics than cocaine, as tested on the cornea of the rabbit. The minimum effective concentration of the best of these, benzylbenzoyl-*d*-ψ-ecgonine, is one-fourth that of cocaine. Five are better anæsthetics than cocaine as tested by subcutaneous injection; of these the best, β-phenylethylbenzoyl-*d*-ψ-ecgonine and α-phenylethylbenzoyl-*l*-ecgonine, are active in one-eighth the concentration required by cocaine. The toxicity of the substances just mentioned, as determined by intravenous injection into mice, is considerably less than that of cocaine in the case of the first, and only slightly greater than that of cocaine in the second and third. Apart from these,

a rough parallelism is observable between degree of anæsthetic action and toxicity. It has been stated that the function of the alkyl ester group is merely the removal of acidic character, the nature of the alcohol used being of no consequence (Fränkel, "Die Arzneimittel Synthese," Berlin, 1921, pp. 335, 353). The results tabulated below show, on the contrary, that changes in this group may exert a notable influence on pharmacological action. Three compounds belonging to a homologous series, *viz.*, benzyl, β-phenylethyl, and γ-phenyl-*n*-propyl esters of benzoyl-*l*-ecgonine, were prepared, and it was found that the anæsthetic effect falls off suddenly after the second member of the series is passed. In other instances in which pharmacological effect has been correlated with length of side-chain, for example, the sympathomimetic action of the phenylalkylamines (Barger and Dale, *J. Physiol.*, 1910, **41**, 19) and the disinfectant action of the alkyl hydrocupreines (Schaeffer, *Biochem. Z.*, 1917, **83**, 269), a similar effect has been noticed. The benzoyl-*d*-ψ-ecgonine esters were more active than their isomerides, thus falling into line with the corresponding *d*-ψ-cocaine (compare Gottlieb, *Arch. exper. Path. Pharmakol.*, 1923, **97**, 113). The ester of secondary phenylethyl alcohol (III) was more active than that of the corresponding primary alcohol and slightly less toxic. It may be noted that the three esters with acyl groups other than benzoyl provide no exception to the rule indicated in the second paragraph, although the salicyloyl compound is a more active surface anæsthetic than cocaine.

TABLE.

The substances are arranged in order of decreasing action on the cornea, in percentage strength of aqueous solutions of a salt. Toxicities are expressed in mg./kilo of body-weight required to kill 50% of the mice used.

Name.	Minimum effective concentration. *Corneal.*	*Subcutaneous.*	Average lethal dose.
Benzylbenzoyl-*d*-ψ-ecgonine *	0·05—0·025	0·01 —0·005	39
β-Phenylethylbenzoyl-*d*-ψ-ecgonine	0·1 —0·05	0·005—0·0025	18
α-Phenylethylbenzoyl-*l*-ecgonine	0·1 —0·05	0·005—0·0025	18
β-Phenylethylbenzoyl-*l*-ecgonine	0·1 —0·05	0·01 —0·005	16·5
Benzylbenzoyl-*l*-ecgonine	0·1 —0·05	0·01 —0·005	33
Benzylsalicyloyl-*l*-ecgonine	0·1 —0·05	0·1 —0·05	*ca.* 90
γ-Phenyl-*n*-propylbenzoyl-*l*-ecgonine	0·1	0·1 —0·05	45·5
o-Hydroxybenzylbenzoyl-*l*-ecgonine	>0·1	>0·1	50
Methylbenzoyl-*l*-ecgonine (cocaine)	0·2 —0·1	0·04	25
Benzyl-2-hydroxy-3-methylbenzoyl-*l*-ecgonine	>0·2	0·2 —0·1	*ca.* 50
p-Nitrobenzylbenzoyl-*l*-ecgonine	>0·5	0·1 —0·05	*ca.* 50
Benzyltropoyl-*l*-ecgonine	1·0 —0·5	0·05 —0·025	*ca.* 40

* Subsequent to the completion of this work a paper has appeared (Poulsson and Wiedemann, *Arch. exper. Path. Pharmakol.*, 1925, **105**, 58) in which the preparation of a benzylbenzoylecgonine is described; the melting point of the hydrochloride is, however, considerably lower than that of ours.

EXPERIMENTAL.

The esters of benzoyl-*l*-ecgonine were prepared, in general, by heating an intimate mixture of benzoyl-*l*-ecgonine (1 mol.), powdered sodium hydroxide (1 mol.), excess of appropriate aralkyl chloride (3 mols.), and a small quantity of pyridine. The pasty reaction mixture was stirred frequently and heated for 7 hours at suitable temperatures ranging from 90° to 120°. The cooled product was treated with dilute acid and freed from aralkyl chloride by agitation with ether; after saturation with sodium bicarbonate, the new base was extracted with ether and purified by means of a salt.

The esters of the other acylecgonines were more conveniently made by the converse procedure, as follows. The hydrochloride of *l*-ecgonine or *d*-ψ-ecgonine was first treated in the manner just described with aralkyl chloride and sodium hydroxide (2 mols.), which converted it into the corresponding alkylecgonine, which was soluble in organic solvents. This base was then acylated by the appropriate reagent, for instance, benzoic anhydride in benzene solution.

Benzylbenzoyl-1-ecgonine.—Benzoylecgonine (12 g.), powdered sodium hydroxide (1·33 g.), benzyl chloride (13·3 c.c.), and pyridine (1·7 c.c.) were thoroughly mixed and treated as above, yielding 10·6 g. of base as a thick oil with a tropine-like odour. It could not be crystallised and was purified for analysis by regeneration from the hydrochloride (Found: C, 73·1; H, 6·9; N, 3·6. $C_{23}H_{25}O_4N$ requires C, 72·8; H, 6·6; N, 3·7%). The *hydrochloride* crystallises from dry acetone in lustrous, six-sided leaflets, m. p. 171° (corr.), soluble in its own weight of water, readily soluble in alcohol, and sparingly soluble in acetone; $[\alpha]_D$ –18·62° in 2% aqueous solution. The dilute aqueous solution causes persistent numbness when placed on the tongue. The yield of the pure salt was 51% of the benzoylecgonine taken (Found: Cl, 8·5. $C_{23}H_{25}O_4N,HCl$ requires Cl, 8·5%). The *nitrate* crystallises from acetone in fine needles, m. p. 163° (corr.; decomp.) (Found: C, 61·9; H, 5·9; N, 6·4. $C_{23}H_{25}O_4N,HNO_3$ requires C, 62·4; H, 5·9; N, 6·3%). The *hydrogen sulphate* is insoluble in acetone. It crystallises from alcohol in clusters of rectangular plates, m. p. 206—208° (corr.). (Found: S, 6·55. $C_{23}H_{25}O_4N,H_2SO_4$ requires S, 6·7%). The *chloroaurate* crystallises from boiling methyl alcohol, in which it is sparingly soluble, in large, glistening plates, m. p. 111° (corr.), insoluble in water, ethyl alcohol, or petroleum, readily soluble in chloroform or acetone. (Found: Au, 27·8. $C_{23}H_{25}O_4N,HCl,AuCl_3$ requires Au, 27·4%). The *chloroplatinate* is precipitated from aqueous solutions in minute needles, m. p. 210° (corr.), with two molecules of water of crystallisation, which it loses at 60° in a vacuum.

The dried substance melts at 211° (corr.) [Found: loss at 60°, 3·4. $(C_{23}H_{25}O_4N,HCl)_2,PtCl_4,2H_2O$ requires H_2O, 3·0%. Found, in the dried substance: Pt, 16·7. $(C_{23}H_{25}O_4N,HCl)_2,PtCl_4$ requires Pt, 16·7%]. The *picrate*, precipitated from aqueous solutions, separates from hot absolute alcohol as an oil, slowly changing on standing into clumps of needles, m. p. 80° [Found: N, 9·15. $C_{23}H_{25}O_4N,C_6H_2(NO_2)_3\cdot OH$ requires N, 9·2%.]

p-*Nitrobenzylbenzoyl-l-ecgonine*.—As the esterification appeared to proceed with unusual readiness in this case, the action of *p*-nitrobenzyl chloride on cocaine was tried under similar conditions, to ascertain if interchange of ester groups would take place. Considerable tar formation occurred, however, and the only product isolated was unchanged cocaine.

Benzoylecgonine (12 g.), sodium hydroxide (1·3 g.), *p*-nitrobenzyl chloride (20 g.), and pyridine (1·3 c.c.) yielded by the standard procedure 12 g. of base, which did not crystallise, and was purified by means of its hydrochloride (Found: C, 64·9; H, 5·8; N, 6·6. $C_{23}H_{24}O_6N_2$ requires C, 65·1; H, 5·7; N, 6·6%). The crude crystalline *hydrochloride*, after being washed with cold acetone to remove a coloured impurity, crystallised from boiling acetone in minute leaflets, m. p. 178·5° (corr.). It is soluble in 40 parts of water at 15°, readily soluble in chloroform, sparingly soluble in alcohol or acetone; $[\alpha]_D$ + 17·98° in 2% aqueous solution (Found: Cl, 7·6. $C_{23}H_{24}O_6N_2,HCl$ requires Cl, 7·7%). The *nitrate* was precipitated from a solution of the hydrochloride by dilute nitric acid in fine, silky needles, m. p. 187° (corr.), and was almost insoluble in water (Found: C, 56·4; H, 5·3; N, 8·7. $C_{23}H_{24}O_6N_2,HNO_3$ requires C, 56·7; H, 5·4; N, 8·6%). The *hydrogen sulphate* is prepared similarly, but needed to be recrystallised from alcohol; needles, m. p. 195° (corr.) (Found: S, 6·3. $C_{23}H_{24}O_6N_2,H_2SO_4$ requires S, 6·1%). The *chloroaurate* crystallises from methyl alcohol in well-formed prisms, m. p. 154° (corr.) (Found: Au, 25·8. $C_{23}H_{24}O_6N_2,HCl,AuCl_3$ requires Au, 25·8%). The *chloroplatinate* is practically insoluble in methyl or ethyl alcohol, and crystallises from hot water in glistening, elongated plates, m. p. 204—205° (corr.; decomp.). At 60°, this lost $2\frac{1}{2}H_2O$ and then melted at 210° (corr.) [Found: loss at 60°, 3·6. $(C_{23}H_{24}O_6N_2,HCl)_2,PtCl_4,2\frac{1}{2}H_2O$ requires H_2O, 3·45%. Found, in the dried substance; Pt, 15·6. $(C_{23}H_{24}O_6N_2,HCl)_2,PtCl_4$ requires Pt, 15·5%]. The *picrate* crystallises from alcohol in clusters of fine needles, m. p. 84° (corr.) [Found: N, 10·8. $C_{23}H_{24}O_6N_2,C_6H_2(NO_2)_3\cdot OH$ requires N, 10·7%].

Attempts were made to reduce this substance to the corresponding amino-ester; a number of reducing agents were tried, but in no case was the desired product obtained.

o-Hydroxybenzylbenzoyl-l-ecgonine.—Attempts to prepare *o*-hydroxybenzyl chloride from saligenin led only to copious tar formation, and the alternative of acting upon saligenin with an acid chloride of ecgonine or benzoylecgonine was not realised; by the action of thionyl chloride on these bases only their hydrochlorides could be isolated. Interchange of ester groups did not occur when saligenin and cocaine were heated together, unchanged cocaine being recovered or resinous products formed according to the temperature employed. The ester was finally obtained by the use of *o-acetoxybenzyl chloride*, the acetyl group being removed without special treatment during the purification process. This substance, the preparation of which does not appear to have been described, was obtained as follows. Monoacetylsaligenin (Hart and Hirschfelder, *J. Amer. Chem. Soc.*, 1921, **43**, 1688) (26·8 g.) was dissolved in an equal volume of diethylaniline and treated with thionyl chloride (14 c.c.). After standing over-night, the mixture was heated at 110—120° for 8½ hours and worked up according to the procedure of Darzens for phenylethyl chloride (*Compt. rend.*, 1911, **152**, 1314). The chloride is a colourless oil with a faint, pleasant smell, b. p. 135°/14 mm. (Found: C, 59·0; H, 5·2. $C_9H_9O_2Cl$ requires C, 58·5; H, 4·9%). For preparation of the ester the fraction collected over 142—150°/20 mm. was used without further purification, 9·6 g. being treated as above with benzoylecgonine (6 g.), sodium hydroxide (0·7 g.), and pyridine (0·15 c.c.), yielding 6 g. of oil, which was purified by conversion into the hydrochloride and treatment of this with ether. Neither the base nor the hydrochloride was obtained crystalline (Found: C, 69·1; H, 6·6; N, 3·6. $C_{23}H_{25}O_5N$ requires C, 69·85; H, 6·4; N, 3·6%). The *picrate* was dried for analysis at 60° in a vacuum [Found: N, 9·2. $C_{23}H_{25}O_5N,C_6H_2(NO_2)_3\cdot OH$ requires N, 9·0%).

β-Phenylethylbenzoyl-l-ecgonine.—Benzoylecgonine (10·1 g.), sodium hydroxide (1·08 g.), phenylethyl chloride (17·1 c.c.) (Darzens, *loc. cit.*), and pyridine (1·5 c.c.) were heated together at 120°; at a lower temperature, the yield was unsatisfactory. The base crystallised directly on evaporation of the dried ethereal extract, in rosettes of needles, m. p. 100° (corr.) after recrystallisation from alcohol (Found: C, 73·1; H, 7·1; N, 3·7. $C_{24}H_{27}O_4N$ requires C, 73·3; H, 6·9; N, 3·6%). The *hydrochloride* crystallises from dry acetone in elongated, flattened prisms, m. p. 196° (corr.), readily soluble in water or alcohol, sparingly soluble in acetone; $[\alpha]_D$ −39·2° in 2% aqueous solution (Found: Cl, 8·3. $C_{24}H_{27}O_4N,HCl$ requires Cl, 8·25%). The *chloroplatinate* crystallises from methyl alcohol in delicate, six-sided plates, m. p. 216° (corr.) [Found: Pt, 16·4. $(C_{24}H_{27}O_4N,HCl)_2,PtCl_4$ requires Pt, 16·3%]. The *picrate* was precipitated from aqueous solutions as a granular solid, m. p. 66°

(corr.) [Found: N, 9·0. $C_{24}H_{27}O_4N,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 9·0%].

*α-Phenylethylbenzoyl-*l*-ecgonine.*—Phenylmethylcarbinol, obtained by reduction of acetophenone (Klages and Allendorff, *Ber.*, 1898, **31**, 1003) gave a moderate yield of the corresponding chloride by the thionyl chloride method, but a much better result by treatment with calcium chloride and dry hydrogen chloride (Engler and Bethge, *Ber.*, 1874, 7, 1127). A temperature above 100° could not be employed in the esterification, hydrogen chloride being evolved and a very poor yield obtained. The reaction proceeded slowly at 100°, heating for several days being required. In this case the product was first treated with acetone, unchanged benzoylecgonine hydrochloride remaining undissolved. 12·8 C.c. of α-chloroethylbenzene and 7·6 g. of benzoylecgonine yielded in this way 5·0 g. of pure base as an oil (Found: C, 72·95; H, 7·2; N, 3·6. $C_{24}H_{27}O_4N$ requires C, 73·3; H, 6·9; N, 3·6%). The *hydrochloride* is extremely deliquescent; it may be precipitated as a solid by mixing solutions of the base and hydrogen chloride in dry ether, and is readily soluble in acetone. The *hydrobromide* and *nitrate* are also very deliquescent. The *chloroaurate* crystallises from alcohol in clusters of thin plates, m. p. 170° (corr.). It is more readily soluble in organic solvents than the other chloroaurates described in this paper (Found: Au, 26·9. $C_{24}H_{27}O_4N,HCl,AuCl_3$ requires Au, 26·9%).

*Phenyl-*n*-propylbenzoyl-*l*-ecgonine.*—γ-Phenyl-*n*-propyl alcohol was prepared by running a mixture of cinnamyl alcohol and absolute alcohol (1 mol.) on to freshly-cut sodium at 100°. Phenylpropyl chloride (10·3 g.), prepared from this by the thionyl chloride method (see above), benzoylecgonine (5·54 g.), sodium hydroxide (0·59 g.), and pyridine (0·8 c.c.) yielded, at 120°, 5·9 g. of crude base. Impurities were removed by extracting the aqueous hydrochloride solution with ether, and 5·6 g. of pure base recovered as an oil (Found: C, 73·5; H, 7·25; N, 3·4. $C_{25}H_{29}O_4N$ requires C, 73·65; H, 7·2; N, 3·4%). The *hydrochloride* was not obtained crystalline.

*Benzyltropoyl-*l*-ecgonine.*—Treatment of ecgonine hydrochloride with acetyltropyl chloride (compare the partial synthesis of atropine by Wolffenstein and Mamlock, *Ber.*, 1908, **41**, 723), followed by esterification of the resulting product, gave a small yield of base soluble in ether, but a much better result was obtained by first benzylating the ecgonine, and treating the base so obtained with acetyltropyl chloride. Ecgonine hydrochloride (8·8 g.) and benzyl chloride (16 c.c.) gave by the standard procedure 7·7 g. of ether-soluble base, which, without further purification, was heated with the acetylchloride from 8 g. of tropic acid (Wolffenstein and Mamlock, *loc. cit.*). The tough solid obtained was purified by repeated

solution in acetone and precipitation with ether, and yielded 6·2 g. of base as an uncrystallisable oil (Found: C, 71·1; H, 7·1; N, 3·4. $C_{25}H_{29}O_5N$ requires C, 70·9; H, 6·9; N, 3·3%). The hydrochloride also was an oil, soluble with difficulty in water; for the preparation of the salts and for physiological testing, a solution of the lactate was used. The *chloroaurate* formed small needles, m. p. 90° (corr.) (Found: Au, 25·2. $C_{25}H_{29}O_5N,HCl,AuCl_3$ requires Au, 25·8%). The *picrate* is a granular solid, m. p. 65° (corr.) [Found: N = 8·7. $C_{25}H_{29}O_5N,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 8·6%].

Benzyl-o-hydroxybenzoyl-l-ecgonine.—Sodium salicylate (12·8 g.) was converted into salicyloyl chloride (Kopetschni and Karczag, D.R.-P. 262883) and heated at 100° under reduced pressure with benzylecgonine (6·6 g.), prepared as described above, for 2 hours. The product was dissolved in water and purified by agitation with ether, 5·3 g. of base being obtained. Neither this nor the hydrochloride could be crystallised and the base was purified through the *picrate*, small columns, m. p. 67° (corr.) [Found: N, 8·9. $C_{23}H_{25}O_5N,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 9·0%. Found, on the base: C, 70·3; H, 6·5; N, 3·5. $C_{23}H_{25}O_5N$ requires C, 69·85; H, 6·4; N, 3·5%].

Benzyl-2-hydroxy-3-methylbenzoyl-l-ecgonine.—This and the following base were prepared from sodium *o*- and *m*-hydroxytoluates respectively in the same way as benzyl-*o*-hydroxybenzoyl-*l*-ecgonine. They were not obtained crystalline, and were purified by means of their picrates (Found: C, 70·3; H, 6·8; N, 3·5. $C_{24}H_{27}O_5N$ requires C, 70·4; H, 6·65; N, 3·4%). The *picrate* is a granular solid, m. p. 67° (corr.) [Found: N, 8·8. $C_{24}H_{27}O_5N,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 8·8%].

Benzyl-2-hydroxy-4-methylbenzoyl-l-ecgonine (Found: C, 70·3; H, 6·8; N, 3·4. $C_{24}H_{27}O_5N$ requires C, 70·4; H, 6·65; N, 3·4%). The *picrate* is a granular solid, m. p. 70° (corr.) [Found: N, 8·8. $C_{24}H_{27}O_5N,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 8·8%].

Benzylbenzoyl-d-ψ-ecgonine.—Poor yields of benzoyl-*d*-ψ-ecgonine were obtained by the procedure of D. R.-P. 55338, or when *d*-ψ-ecgonine was treated with benzoyl chloride. *d*-ψ-Ecgonine hydrochloride (3·2 g.), benzyl chloride (6 c.c), sodium hydroxide (1·2 g.), and pyridine (0·6 c.c.) reacted vigorously at 150° and yielded, after heating for ½ hour, 2·8 g. of benzyl-*d*-ψ-ecgonine as an oil, soluble in organic solvents. This base (3·6 g.) was dissolved in an equal weight of dry benzene and heated under reflux with benzoic anhydride (9·2 g.) for 6 hours, 35 c.c. of ether were then added, and the filtered solution was shaken with 30 c.c. of 7% hydrochloric acid. A copious separation of glistening platelets, m. p. 211° (corr.), of benzylbenzoyl-*d*-ψ-ecgonine hydrochloride occurred (yield 2·53 g.),

from which the base was obtained as a colourless oil by agitation with sodium bicarbonate solution and ether (Found: C, 72·6; H, 7·0; N, 3·7. $C_{23}H_{25}O_4N$ requires C, 72·8; H, 6·6; N, 3·7%). The *hydrochloride*, obtained as already described, was washed free from traces of colouring matter by cold dry acetone, in which it is almost insoluble; m. p. 213° (corr.). It is readily soluble in hot water, but very sparingly soluble at 20° (Found: Cl, 8·55. $C_{23}H_{25}O_4N,HCl$ requires Cl, 8·5%). The *nitrate* crystallises from dilute alcohol in small, square plates, m. p. 168° (corr.) (Found: C, 62·4; H, 6·2; N, 6·4. $C_{23}H_{25}O_4N,HNO_3$ requires C, 62·4; H, 5·9; N, 6·3%). The neutral *tartrate* crystallises from water, in which it is moderately soluble, in fine needles, m. p. 155° (corr.). It is readily soluble in alcohol. The *mucate* forms felted needles, m. p. 142–143° (corr.), very sparingly soluble in cold water. The *picrate* is precipitated from aqueous solutions as a granular solid, m. p. 80° (corr.) [Found: N, 9·2. $C_{23}H_{25}O_4N,C_6H_2(NO_2)_3\cdot OH$ requires N, 9·2 %].

β-*Phenylethylbenzoyl*-d-*ψ*-*ecgonine* was prepared in the same way as the preceding ester, but the hydrochloride was more soluble and did not crystallise directly. 5·5 Grams of *d*-*ψ*-ecgonine hydrochloride yielded 5·7 g. of base, which, after purification by means of the hydrochloride, crystallised in square plates, m. p. 63° (corr.) (Found: C, 73·3; H, 6·9; N, 3·5. $C_{24}H_{27}O_4N$ requires C, 73·3; H, 6·9; N, 3·6%). The *hydrochloride* crystallises from acetone in silky needles, m. p. 197° (corr.), soluble in 89·6 parts of water at 16°; $[\alpha]_D$ + 35·0° in 1% aqueous solution (Found: Cl, 8·35. $C_{24}H_{27}O_4N,HCl$ requires Cl, 8·25%).

In conclusion, the author desires to express his warmest thanks to Dr. T. A. Henry for his advice and criticism, and to Mr. W. Ramsay for assistance in the experimental work.

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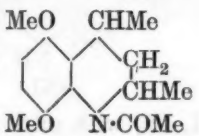
LONDON, E.C. 1. [*Received, March 19th*, 1925.]

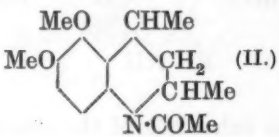
CLXI.—*Strychnine and Brucine. Part III. The Position of the Methoxyl Groups in Brucine.*

By FRANCIS LIONS, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

THE first clear evidence that the molecule of brucine contains two methoxyl groups in an aromatic nucleus which are in the ortho- or para-positions to each other was furnished by Leuchs and Geiger

(*Ber.*, 1909, **42**, 3067), who showed that a brucinesulphonic acid is changed by nitric acid to a related quinone and a nitro-quinone by simultaneous oxidation and demethylation with or without nitration. This was followed by numerous similar observations on the part of Leuchs and his co-workers. Thus Leuchs and Weber (*Ber.*, 1909, 42, 3703) obtained a quinone and corresponding quinol from brucinolone, and Leuchs and Anderson (*Ber.*, 1911, **44**, 2136) prepared bis*apo*methylbrucine itself. On the assumption that brucine is a dimethoxytetrahydroquinoline derivative, Tafel and Moufang (*Annalen*, 1899, **304**, 25) expressed the opinion that one of the methoxyls occupies the position in the benzene ring para to the nitrogen atom, but there is no proof of this and the position occupied by these groups is not indicated by any degradation product of brucine as yet obtained. It occurred to us that, since the brucine–nitric acid reaction is so characteristic, some indirect but nevertheless valuable information might be gleaned from the study of the behaviour with nitric acid of synthetical compounds containing methoxyl groups oriented so as to be typical of the various possibilities which must be considered in the case of brucine. The series which we chose for examination was that of the *N*-acetyldimethoxydimethyltetrahydroquinolines (I, II, III, IV), which were

(I.) 



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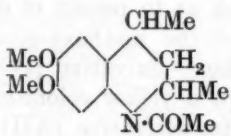
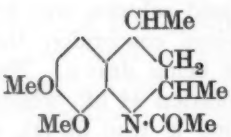
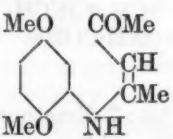
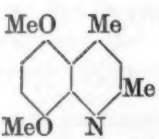
(III.) 



(IV.)

obtained by the following methods. Aminoquinol dimethyl ether condenses with acetylacetone to form an intermediate (V) which is changed by sulphuric acid to 5 : 8-dimethoxy-2 : 4-dimethylquinoline (VI).

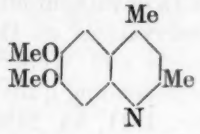
(V.) 

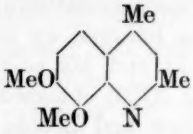


(VI.)

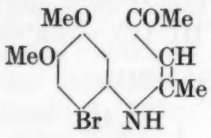
Similarly, 4-aminoveratrole yields the quinoline (VII) and the *N*-acetyltetrahydro-derivative (III), whilst (VIII) and (IV) are as readily obtained from 3-aminoveratrole. It was more difficult to

obtain a 5 : 6-dimethoxyquinoline derivative not containing a substituent in position 8, but the preparation of the compound (II)

(VII.) 

 (VIII.)

was ultimately achieved by blocking position 8 with a bromine atom which could subsequently be removed by reduction. 5-Bromo-4-aminoveratrole and acetylacetone yield the substituted anilide (IX), which may be dehydrated by careful treatment with concentrated sulphuric acid so as to produce a bromodimethoxydimethylquinoline (X). On reduction with sodium and alcohol, a bromine-free dimethoxydimethyltetrahydroquinoline (XI) is obtained. Unfortunately the acetyl derivative (II) could not be crystallised and it may be mentioned that, on account of the stereoisomerism which is due to the existence of the methyl groups in the *cis*- and *trans*-positions in the tetrahydroquinolines, poor yields of homogeneous, crystalline acetyl derivatives were obtained in all cases.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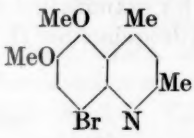
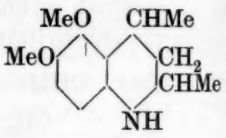
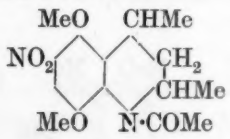
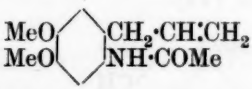

(X.)


(XI.)

The behaviour of the standards (I, II, III, IV) with nitric acid in acetic acid solution was fortunately such as to permit of definite conclusions concerning the positions of the methoxy-groups in brucine being drawn. The 7 : 8-dimethoxy-derivative (IV) gives no coloration at all, whilst (II) develops a yellow coloration and the same is true of (I), a definite nitro-derivative (XII) being isolated in this case. Brucine cannot, therefore, have the arrangement of methoxyl groups proposed in Part I (Perkin and Robinson, J., 1910, **97**, 305).

(XII.) 

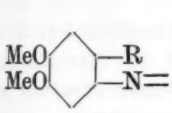
 (XIII.)

The remaining isomeride, namely, *N*-acetyl-6 : 7-dimethoxy-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (III), exhibits a reaction with nitric acid which is almost identical in colour and tone and persistence on dilution with that characteristic of brucine. We then experimented with similarly constituted amides and found

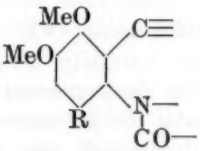
that this reaction is given by 5-bromo-4-acetylaminoveratrole (Jones and Robinson, J., 1917, **111**, 903), 6-acetylaminohomoveratrole (Luff, Perkin, and Robinson, J., 1910, **97**, 1131), acetylaminosafrole (Foulds and Robinson, J, 1914, **105**, 1963), and 5-acetylamino-4-allylveratrole (XIII). It appears, therefore, that 6-substituted-3 : 4-dialkyloxyacylanilides exhibit the nitric acid reaction of brucine. There is, nevertheless, one important difference, and that is the very much greater delicacy of the reaction in the case of brucine. The orange-red colour is produced with the alkaloid in acetic acid solution with concentrations of nitric acid which leave the synthetical compounds quite unchanged. Great significance undoubtedly attaches to this fact and it is for this reason that we state our conclusions from these experiments in the following propositions.

(1) Brucine contains two methoxyl groups in the ortho-position to each other in a benzene ring, and the quinones from brucine and its derivatives are *o*-quinones.

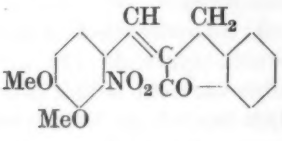
(2) If brucine contains a benzene ring bearing only *four substituents*, then these are arranged as shown in the expression XIV.



(XIV.)



(XV.)



(XVI.)

(3) In case the benzene ring bears more than four substituents, such arrangements as XV are possible. An alternative statement is that there can be no unsubstituted position in the benzene nucleus para to either of the methoxyl groups. The schemes given by Leuchs and Taube (*Ber.*, 1924, **57**, 1092) to represent the possible course of the opening of the benzene ring of cacothelin under the influence of bromine can only with difficulty be reconciled with the above conclusions, although the final result can readily be explained. In considering the mechanism of the process the possibility of molecular rearrangement must not be overlooked in the case of a molecule containing so many oxygen and bromine atoms at close quarters. Finally, we were unable to reduce 2′-nitro-3′ : 4′-dimethoxy-2-benzylidene-1-hydrindone (XVI) to a quinoline derivative, although the process works well with the related 6-nitropiperonylidenehydrindone (Armit and Robinson, J., 1922, **121**, 831). This result is clearly due to steric hindrance exerted on the nitro-group, and a quite similar case has been recorded by Rilliet (*Helv. Chim. Acta*, 1922, **5**, 547). 6-Nitroveratrylidene-*p*-toluidine

can be readily reduced by aqueous alcoholic sodium sulphide to an amino-derivative, but this was not found possible in the case of the Schiff base derived from 2-nitroveratraldehyde.

EXPERIMENTAL.

β-2 : 5-*Dimethoxyanilinopropenyl Methyl Ketone* (V).—2 : 5-Dimethoxyaniline is best obtained by reduction of nitroquinol dimethyl ether with iron filings and dilute acetic acid at 80—95° in a digester fitted with two propeller blades revolving in opposite directions. Almost 60% is obtained in snow-white crystals by steam distillation, and a further 30% may be recovered from the aqueous distillate by extraction with benzene. A mixture of the base (45 g.) and acetylacetone (32 g.) was gently boiled under reflux for 30 minutes, and the product, washed with water, was collected by ether. The dry residue (58 g.) was a brown oil which gradually crystallised. The compound is readily soluble in most organic solvents, but can be crystallised from ether in colourless, hexagonal plates, m. p. 55° (Found: C, 66·5; H, 7·4. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·3%). The substance is readily hydrolysed by dilute acids, yielding its generators.

5 : 8-*Dimethoxy*-2 : 4-*dimethylquinoline* (VI).—Acetylacetone-2 : 5-dimethoxyanilide (30 g.) was carefully added to concentrated sulphuric acid (180 g.), and the dark greenish-yellow solution was then heated on the steam-bath for 10 minutes and poured into water. On cooling, the sulphate of the quinoline derivative separated in bright yellow needles, and on the addition of sodium hydroxide the *base* itself was obtained as a grey solid (24 g.), which was crystallised from aqueous alcohol and from ethyl acetate (Found: C, 71·8; H, 6·8. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 7·0%). The base is readily soluble in the simple alcohols, moderately soluble in benzene or chloroform, and but sparingly soluble in ether. It crystallises in slender, colourless needles, m. p. 107°, and is characterised by the intense yellow colour of its salts. The *hydrochloride* is sparingly soluble in cold water and crystallises from acetone in yellow needles, m. p. 235—237° (decomp.). The *picrate*, m. p. 190° with previous darkening, crystallises from alcohol in small, well-defined, yellow prisms.

5 : 8-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (Formula corresponding with I).—Sodium (30 g.), cut in small pieces, was added to a boiling solution of 5 : 8-dimethoxy-2 : 4-dimethylquinoline (20 g.) in absolute ethyl alcohol (300 c.c.) under reflux. When all the metal had disappeared, the alcohol was removed by distillation in steam, and the brown oil which separated was collected and dried in ether and distilled under diminished

pressure, 17 g. of a colourless, viscous oil, b. p. 170—172°/10 mm., being obtained (Found: C, 70·3; H, 8·7. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7%). This strong base is volatile in steam to some extent and is odourless. A solution of its hydrochloride gives no colour with ferric chloride in the cold, but, on warming, a permanganate colour develops and this fades to reddish-brown. It gives a dark blood-red coloration with concentrated nitric acid or with dilute nitric acid and a trace of sodium nitrite.

The N-*acetyl* derivative (I) was prepared by acetylating the base with twice its weight of acetic anhydride for 2 hours in the cold and then for 15 minutes on the steam-bath. The excess of reagent was decomposed by dilute hydrochloric acid, and the oil washed with water and dried; after 3 days, the material had largely solidified. The substance crystallised from benzene–ligroin in small, colourless, rhombic plates, m. p. 85—86° (Found: C, 68·2; H, 8·1. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). The yield was less than 60% and the mother-liquors contained an uncrystallisable oil. This derivative is readily soluble in most organic solvents. It dissolves in sulphuric acid to a yellowish-green solution which changes to green and then to brown; on heating, the colour changes are through brown to reddish-violet, red, and orange.

6-*Nitro*-1-*acetyl*-5 : 8-*dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XII).—1-Acetyl-5 : 8-dimethoxy-2 : 4-dimethyltetrahydroquinoline (2 g.) was dissolved in acetic acid (15 c.c.), and nitric acid (4 c.c.; *d* 1·42) gradually introduced. After an hour the mixture was added to water, and the yellow solid was washed and dried (2 g.) (Found: C, 58·3; H, 6·8. $C_{15}H_{20}O_5N_2$ requires C, 58·4; H, 6·5%). The substance is readily soluble in most organic solvents and crystallises in stellar aggregates of long, flat, needles, m. p. 127°, from a mixture of ethyl acetate and ligroin. The yellow solution in sulphuric acid remains unchanged on the addition of a trace of potassium dichromate and this indicates that the *p*-position to the quinoline nitrogen is occupied.

6-*Acetylamino*-1-*acetyl*-5 : 8-*dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*.—Nitro-1-acetyldimethoxydimethyltetrahydroquinoline (1 g.) was gradually introduced into a well-stirred mixture of acetic acid (0·2 c.c.), iron filings (10 g.), and water (25 c.c.) at 80—90°, and the agitation continued for an hour. Alternatively, reduction may be effected with boiling aqueous sodium sulphide. In either case, a brown basic oil could be isolated, but could not be induced to crystallise. It reacted vigorously with acetic anhydride, a white, crystalline powder separating at once. This derivative crystallises from ethyl acetate–light petroleum in small,

colourless prisms, m. p. 171° (Found : C, 63·7; H, 7·4. $C_{17}H_{24}O_4N_2$ requires C, 63·7; H, 7·6%).

β-6-*Bromo*-3 : 4-*dimethoxyanilinopropenyl Methyl Ketone* (IX).—In the preparation of 5-bromo-4-aminoveratrole by the hydrolysis of its acetyl derivative with methyl-alcoholic potassium hydroxide (Jones and Robinson, J., 1917, **111**, 913; Simonsen and Rau, J., 1918, **113**, 787) we have found a modification of the isolation process serviceable. After the hydrolysis the excess of alkali is neutralised with carbon dioxide, and the filtered solution, cooled in ice, is treated with a slight excess of hydrochloric acid. The *hydrochloride* of the base which separates is washed with alcohol until colourless and dried, the yield being satisfactory. This salt crystallises from methyl alcohol in lustrous prisms, m. p. 216—218° (decomp.). It is sparingly soluble in cold water, but if the solution be heated, decomposition occurs and a deep purple coloration is soon produced. This is, of course, traceable to the presence of a *positive* bromine atom, the activation of which is due to the amino-group in the *o*-position. A striking confirmation of this view is to be found in the fact that a solution of the salt in moderately concentrated hydrochloric acid can be boiled without decomposition. In view of this curious decomposition,* the base was set free from a *cold* dilute solution of the hydrochloride by means of sodium hydroxide. This instability of the bromoaminoveratrole necessitates the observance of precautions against overheating in the course of its condensation with acetylacetone, failing which, rapid and complete decomposition ensues. A mixture of the base (23 g.) and acetylacetone (15 g.) was gently boiled for 10 minutes, and the dark, purplish-red product washed with water, dried, and the solvent removed, leaving an oily residue which slowly crystallised. The substance is readily soluble in the common organic solvents with the exception of light petroleum and crystallises from aqueous alcohol in nearly colourless needles, m. p. 78—79° (Found : C, 50·4; H, 5·4. $C_{13}H_{16}O_3NBr$ requires C, 49·7; H, 5·1%).

8-*Bromo*-5 : 6-*dimethoxy*-2 : 4-*dimethylquinoline* (X).—This substance is conveniently obtained under the following conditions, which are the result of numerous trials and cannot be usefully varied so far as our experience goes. The acetylacetonebromodimethoxyanilide (10 g.) was gradually added to well-cooled and stirred concentrated sulphuric acid (80 g.) and the mixture was finally heated at 60° for a few minutes and then allowed to remain for ½

* One of the products of the reaction is a neutral substance containing bromine and separating from ethyl acetate as a dark brown, crystalline powder, m. p. 160—161°. This compound dissolves in sulphuric acid to a pure blue solution.

hour. The product was added to ice and water, the cold, dark yellow solution basified with sodium hydroxide, and the solid collected. The solution of the base in hot dilute hydrochloric acid was treated with animal charcoal and the base, again isolated from the lemon-yellow solution, could be crystallised from aqueous methyl alcohol in faintly yellow, slender needles, m. p. 74—75° (yield 70%) (Found : C, 52·2; H, 4·6. $C_{13}H_{14}O_2NBr$ requires C, 52·7; H, 4·7%). The salts of the base are all yellow and the *hydrochloride* crystallises from acetone in small, elongated prisms, m. p. 136—138°.

5 : 6-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XI).—Sodium (10 g.) was gradually added to a boiling solution of 8-bromo-5 : 6-dimethoxy-2 : 4-dimethylquinoline (7 g.) in absolute alcohol (100 c.c.), and when all the metal had disappeared the alcohol was distilled in steam and the base collected by ether. A pale yellow oil (4 g.), b. p. 166—167°/10 mm., was isolated by fractionation (Found : C, 70·5; H, 8·9. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7%). A dilute solution of the hydrochloride of this base gave a beautiful pink coloration changing to wine-red on the addition of ferric chloride. An oily orange-yellow nitrosoamine was precipitated by the addition of sodium nitrite to the very pale yellow solution in dilute nitric acid. The *acetyl* derivative (II) was obtained by a gentle process of acetylation with acetic anhydride, but could not be induced to crystallise. Its solution in sulphuric acid became intense reddish-brown on the addition of a drop of nitric acid, and when the solution in glacial acetic acid was treated with nitric acid a yellow coloration resulted.

β-3 : 4-*Dimethoxyanilinopropenyl Methyl Ketone*.—A mixture of 4-aminoveratrole (45 g.) (compare Fargher, J., 1920, **117**, 865) and acetylacetone (32 g.) was gently boiled for 30 minutes, and the product isolated as in the case of the 5 : 8-isomeride. The substance is readily soluble in most organic solvents except ether and ligroin and may be crystallised from ethyl acetate–ligroin and from ligroin in minute prisms, m. p. 79° (Found : C, 66·2; H, 7·4. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·3%).

6 : 7-*Dimethoxy*-2 : 4-*dimethylquinoline* (VII).—Acetylacetone-3 : 4-dimethoxyanilide (40 g.) was gradually added to cold sulphuric acid (240 g.), and the solution heated for 10 minutes on the steam-bath. The oil, which was obtained from the diluted liquid on basification, crystallised and was collected, washed, and dried (29 g.). The substance is sparingly soluble in ether and ligroin, otherwise readily soluble in organic solvents, and may be conveniently crystallised from dry acetone, separating in small, colourless, rhombic prisms, m. p. 81·5—82° (Found : C, 71·7; H, 7·0. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 7·0%). In contradistinction to

some of the isomeric quinoline derivatives the salts of this substance are colourless. The *hydrochloride* separates from acetone as a white powder, m. p. 286° (decomp.), and the *picrate* crystallises from the same solvent in slender, yellow needles, m. p. 239°, and is very sparingly soluble. Ferric chloride added to acid solutions of the base produces no distinctive reaction.

6 : 7-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (Formula corresponding with III).—6 : 7-Dimethoxydimethylquinoline (20 g.) in boiling absolute alcohol (300 c.c.) was reduced by the gradual addition of sodium (30 g.). When complete solution occurred, the alcohol was removed by distillation in steam, and the pale brown oil collected by ether and distilled under diminished pressure. There resulted 16·5 g. of a viscous, light yellow oil, b. p. 186—189°/12 mm., which on standing crystallised. The substance crystallised from ligroin in colourless, feathery needles, m. p. 73—74° (Found : C, 70·4; H, 8·8. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7%). The golden-yellow *picrate* has m. p. 145° (decomp.). A solution of the base in dilute hydrochloric acid gradually acquires a pure olive-green colour after the addition of ferric chloride. On heating, the colour appears more rapidly and suddenly fades to a pale lemon-yellow. The formation of a yellow *nitrosoamine* was observed.

1-*Acetyl*-6 : 7-*dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (III).—A solution of the 6 : 7-dimethoxydimethyltetrahydroquinoline (10 g.) in acetic anhydride (20 g.) was kept for 2 hours and then heated on the steam-bath for 15 minutes. After the product, decomposed by water, had been washed with dilute hydrochloric acid, partial crystallisation occurred and about 5 g. of solid could be collected. The substance crystallised from ligroin (b. p. 70—80°) in colourless, well-formed, rhombic prisms, m. p. 118°, readily soluble in most organic solvents (Found : C, 68·5; H, 8·2. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). The pale yellow solution in sulphuric acid becomes bright orange-red on the addition of a trace of nitric acid, and the reaction is identical with that exhibited by brucine in similar circumstances. The colour fades, however, a little more rapidly than that produced by brucine. If a few drops of nitric acid are added to a solution in acetic acid, the yellow coloration at first obtained rapidly deepens to orange-red and the colour is identical with that produced by brucine when treated in the same way. On dilution, the appearance of the liquid is identical in the two cases. Nevertheless, the brucine reaction is exhibited at much the lower concentration of nitric acid.

β-2 : 3-*Dimethoxyanilinopropenyl Methyl Ketone*.—A mixture of

3-aminoveratrole * (25 g.) and acetylacetone (17 g.) was boiled for a few minutes, and the resulting oil was well washed with water and dried (36 g.) (Found: C, 66·1; H, 7·3. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·3%). This substance could not be crystallised and on exposure to air the pale yellow oil darkened to orange-red.

7 : 8-*Dimethoxy*-2 : 4-*dimethylquinoline* (VIII).—Acetylacetone-2 : 3-dimethoxyanilide (32 g.) was carefully added to cooled and stirred sulphuric acid (160 g.), and the dark brown mixture heated for 10 minutes on the steam-bath. The base was isolated in the usual manner and 25 g. of a pale yellow, viscous oil, b. p. 189—191°/10 mm., were collected (Found: C, 71·6; H, 7·1. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 7·0%). The *hydrochloride* crystallises from acetone in pale yellow prisms, m. p. 145°.

7 : 8-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (Formula corresponding with (IV).—The quinoline derivative (20 g.) just described was reduced by sodium (30 g.) in boiling ethyl-alcoholic solution (300 c.c.), and the tetrahydro-derivative isolated in the usual manner. A colourless oil (18 g.), b. p. 168—170°/12 mm., was obtained (Found: C, 70·3; H, 8·5. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7%).

The reactions of the substance resemble those of the 6 : 7-isomeride. Its N-*acetyl* derivative (IV) was obtained exactly as in other cases, and 10 g. of the base yielded only 5 g. of the solid substance. The latter was several times crystallised from light petroleum and then from aqueous methyl alcohol, separating in colourless needles, m. p. 98—99° (Found: C, 68·3; H, 8·1. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). An alcoholic solution was diluted with water and at first clouded, but on further dilution became clear, and on long standing deposited well-shaped, rhombic plates. The solution in acetic acid gives no coloration on the addition of a little nitric acid and only a pale yellow when a considerable volume of the reagent is introduced.

5-*Nitro*-4-*allylveratrole* (compare formula XIII).—Nitric acid (65 g.; *d* 1·42) was added drop by drop during 30 minutes to a vigorously stirred solution of eugenol methyl ether (80 g.) in acetic acid (320 c.c.), cooled in a mixture of ice and salt. After further stirring and cooling for 3 hours, the mixture was added to 3 litres of water, and the precipitated nitro-derivative washed and dried (80 g.). The substance is readily soluble in most organic solvents, but crystallises from light petroleum in slender, lemon needles, m. p. 44° (Found: C, 59·4; H, 5·6. $C_{11}H_{13}O_4N$ requires C, 59·2;

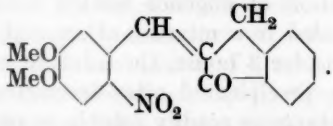
* In the preparation of this base (Gibson, Simonsen, and Rau, J., 1917, 111, 79) by heating 2-amino-3 : 4-dimethoxybenzoic acid with glycerol, mechanical stirring was found to be a considerable advantage.

H, 5·8%).* The solution in concentrated sulphuric acid is bright red.

5-Acetylamino-4-allylveratrole (XIII).—Granulated tin (20 g.) and concentrated hydrochloric acid (30 c.c.) were gradually added to a cooled and agitated mixture of 5-nitro-4-allylveratrole (10 g.), stannous chloride (10 g.), hydrochloric acid (10 c.c.), and acetic acid (35 c.c.), and the stirring was continued until reduction was completed. Zinc was added to eliminate tin, the diluted, filtered solution rendered strongly alkaline with sodium hydroxide, and the oily base (6 g.) collected by ether. When added to twice its weight of acetic anhydride, heat was evolved and the mixture rapidly set to a crystalline mass. The substance was washed, isolated, and crystallised from aqueous methyl alcohol and from ethyl acetate–ligroin, separating in micaceous, colourless needles, m. p. 126—127° (Found: C, 66·0; H, 7·2. $C_{13}H_{17}O_3N$ requires C, 66·3; H, 7·3%). The substance is readily soluble in most organic solvents. A solution of the derivative in sulphuric acid or in acetic acid gives the characteristic brucine orange-red reaction on the addition of nitric acid.

2′-Nitro-3′ : 4′-dimethoxy-2-benzylidene-1-hydrindone (XVI).—A stream of hydrogen chloride was passed through a solution of 2-nitroveratraldehyde (21·1 g.) and α-hydrindone (13·2 g.) in acetic acid (250 c.c.) during 1·5 hours. After several hours, the yellow crystals which had separated were collected and the filtrate was again saturated with hydrogen chloride. This caused a further crystallisation and by repetition of the process 17·8 g. of solid were collected. The substance was several times crystallised from alcohol, in which it was very sparingly soluble, and obtained in yellow prisms, m. p. 156—176° (Found: C, 66·3; H, 4·7. $C_{18}H_{15}O_5N$ requires C, 66·4; H, 4·7%). This material is probably a mixture of stereoisomerides, but it was not found possible to separate these by crystallisation. The solution in sulphuric acid is orange-red. All attempts to obtain a quinoline derivative by reduction were fruitless.

6′-Nitro-3′ : 4′-dimethoxy-2-benzylidene-1-hydrindone,



—This substance was obtained from 6-nitroveratraldehyde in 50% yield by a process exactly similar to that just described in the case of an isomeride. The compound is very sparingly soluble in most

* This substance was first prepared and analysed by Miss E. E. P. Hamilton at the University of Sydney.

organic solvents and is most conveniently crystallised by the addition of alcohol to its solution in hot pyridine, when brownish-yellow needles, m. p. 211°, separate (Found: C, 66·3; H, 4·9. $C_{18}H_{15}O_5N$ requires C, 66·4; H, 4·7%). The solution in sulphuric acid is bright red. By reduction in hot acetic acid solution *dimethoxyindenoquinoline* is produced, the *hydrochloride* of which crystallises from dilute hydrochloric acid in minute prisms, m. p. 251—252° with previous softening, and gives an intensely bluish-purple, fluorescent solution in alcohol. The free base, m. p. 188—190°, crystallises from benzene–ligroin.

The authors desire to thank the Chemical Society for a grant which defrayed a part of the expense of the work, and they are also indebted to the Commissioners of the 1851 Exhibition for a Science Research Scholarship which has enabled one of them (F. L.) to take part in the investigation.

THE UNIVERSITIES OF OXFORD AND MANCHESTER. [*Received, March 21st*, 1925.]

CLXII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXVI. Four Alcohols containing the Vinyl Group and some Esters derived therefrom.*

By JOSEPH KENYON and DOUGLAS ROSEBERY SNELLGROVE.

A LARGE proportion of the work which has hitherto been carried out on the relationship between unsaturation and optical activity suffers from several serious drawbacks which may be classified roughly under three heads:—

1. The compounds examined have frequently been of complicated chemical constitution and have, in addition, possessed one or more of the following disturbing features—

(*a*) have contained more than one asymmetric centre within the molecule,

(*b*) have contained one or more cyclic systems within the molecule,

(*c*) have contained in addition to the ethylenic (or acetylenic) linking other centres of unsaturation such as a phenyl group or a ketonic group.

2. The centre of unsaturation has been remote from the asymmetric carbon atom.

3. The compounds have been solids and their rotatory powers

have necessarily been determined in solution or at high temperatures.

It was therefore considered desirable to prepare optically active compounds each of which should (*a*) be of simple chemical constitution, (*b*) contain only one asymmetric carbon atom, (*c*) contain only one centre of unsaturation, (*d*) have the centre of unsaturation as near as possible to the asymmetric atom, (*e*) be liquid at the ordinary temperature.

With this object in view, the first four members of the homologous series of alcohols of the general formula $CH_2{:}CH{\cdot}CH(OH){\cdot}R$ have been prepared in their optically active modifications. The choice of these alcohols was due, in part, to the fact that the corresponding saturated alcohols, $CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}R$, have already been obtained in their optically active forms (Part IV, J., 1913, **103**, 1923), thus allowing of direct comparisons being made of the effect on rotatory power of an ethylenic linking in each of the four pairs of compounds. The results, which are tabulated below, show that the presence of such linking exalts the rotatory power to a very considerable extent.

Specific Rotatory Powers of the Compounds in the Homogeneous Condition.

Saturated compound.	$[\alpha]_D^{20°}$.		Unsaturated compound.
l-Methylethylcarbinol	−13·9°	−33·7°	*l*-Methylvinylcarbinol
Diethylcarbinol	± 0	−35·2	*l*-Ethylvinylcarbinol
l-*n*-Propylethylcarbinol	− 1·97	−28·2	*l*-*n*-Propylvinylcarbinol
l-*n*-Butylethylcarbinol	− 8·13	−25·0	*l*-*n*-Butylvinylcarbinol *

* Delaby (*Bull. Soc. chim.*, 1923, **33**, 602), by employing the method of resolution used by Pickard and Kenyon, has prepared *l*-*n*-butylvinylcarbinol of $[\alpha]_D^{20°}$ −23·3°. Both *d*- and *l*-forms of this alcohol are described in the present communication with $[\alpha]_D$ ±25·0°. Delaby's paper, which appeared during the course of this work, gives no experimental details of the resolution.

On the other hand, when comparisons are made of the specific rotatory powers of the hydrogen phthalates of these alcohols, the exalting effect of unsaturation on rotatory power becomes much less pronounced, and is in one case entirely suppressed, as is shown by the following results :—

Specific Rotatory Powers of the Hydrogen Phthalates (c = 5 *in Ethyl Alcohol*).

Saturated compound of	$[\alpha]_D$.		Unsaturated compound of
l-Methylethylcarbinol	−38·4°	−40·5°	*l*-Methylvinylcarbinol
Diethylcarbinol	± 0	−26·5	*l*-Ethylvinylcarbinol
l-*n*-Propylethylcarbinol	− 7·26 †	−16·0	*l*-*n*-Propylvinylcarbinol
l-*n*-Butylethylcarbinol	−19·82	−12·6	*l*-*n*-Butylvinylcarbinol

† Compare Part VII, J., 1914, **105**, 2236.

The above table illustrates the need for simplicity of chemical structure in compounds employed in attacking optical problems.

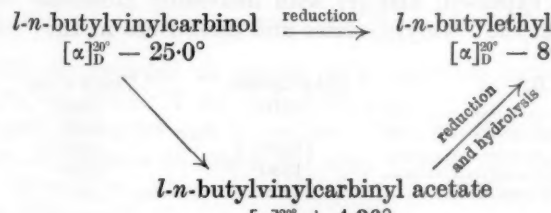
The specific and molecular rotatory powers of ethylvinylcarbinol, which are the highest of the series, are in agreement with the prediction of Frankland (J., 1899, **75**, 868) that some irregularity (maximum or minimum) in rotatory power might be manifested by that member of a homologous series of compounds which contains five carbon atoms. This result is analogous to that shown by *d*-methyl-*n*-propylcarbinol in ethyl-alcoholic solution (Part IV, J., 1913, **103**, 1929); the molecule of each of these alcohols consists essentially of a chain of five carbon atoms.

In order to elucidate the configurational relation between a lævorotatory unsaturated alcohol and the corresponding saturated alcohol of the same sign of rotation, *l*-*n*-butylvinylcarbinol in acetic acid solution was reduced with hydrogen and colloidal platinum. The *l*-*n*-butylethylcarbinol produced was lævorotatory, thus showing that the sign of rotation had not been affected; moreover, the carbinol possessed the same magnitude of rotatory power as the *l*-*n*-butylethylcarbinol prepared by the direct resolution of the *dl*-alcohol.

Some physical properties of the two specimens of this alcohol are compared below :—

	l-Butylethylcarbinol obtained (*a*) by reduction of *l*-butylvinylcarbinol.	(*b*) by direct resolution of *dl*-butylethylcarbinol.
$[\alpha]_D^{20°}$	−8·11°	−8·13°
$d_4^{20°}$	0·8225	0·8227
$n_D^{25°}$	1·4205	1·4204
M. p. of hydrogen phthalate	47—48°	47—48°
$[\alpha]_D^{alc.}$ " " "	−19·84°	−19·82°

Moreover, the acetate of *l*-*n*-butylvinylcarbinol was reduced by the same method; the results are shown by the diagram



In addition to establishing the identity of the reduced alcohol, these data furnish very strong support for the view that optical purity has been reached in the resolution of the alcohols belonging to both these homologous series: the probability that (incomplete)

resolution would take place to exactly the same extent in the cases of *l*-butylvinylcarbinol and *l*-butylethylcarbinol must be exceedingly small.

The rotatory powers of unsaturated compounds hitherto have been determined almost entirely with light of one wave-length—the D line, so that the optical rotatory dispersion of unsaturated compounds of simple chemical constitution is a subject about which little is known. It became, therefore, of particular interest to measure the optical rotatory dispersion of these four unsaturated alcohols. In each case there was sufficient alcohol to fill a 2-dcm. tube, and the rotatory powers were measured for light of wave-lengths ranging from $\lambda = 6708$ to $\lambda = 3780$ Å.U. The rotatory powers were measured also of the alcohols in the homogeneous state at temperatures between 20° and the boiling points.

By applying to the observed rotatory powers the method of calculation used by Lowry in the case of *sec.*-octyl alcohol (J., 1924, **125**, 1596) dispersion equations have been obtained and also values for the constants k_0 and λ_0, for the four alcohols. A one-term dispersion equation containing the calculated values for the "constants" gives rotatory powers in agreement with the experimental data in each case, thus showing that the alcohols possess simple rotatory dispersion within the experimental range.

The equations are:—

		Å. U.
d-Methylvinylcarbinol:	$[\alpha]_{\lambda}^{18°} = 9{\cdot}920/(\lambda^2 - 0{\cdot}0528)\ \lambda_0 =$	2300
d-Ethylvinylcarbinol:	$= 10{\cdot}27/(\lambda^2 - 0{\cdot}0554) =$	2380
l-*n*-Propylvinylcarbinol:	$= 8{\cdot}331/(\lambda^2 - 0{\cdot}0574) =$	2400
d-*n*-Butylvinylcarbinol:	$= 7{\cdot}533/(\lambda^2 - 0{\cdot}0582) =$	2410
d-*n*-Butylvinylcarbinol in *cyclo*hexane solution:	$= 7{\cdot}787/(\lambda^2 - 0{\cdot}0573) =$	2400

On comparing the values of λ_0 for these alcohols with corresponding values for the saturated alcohols, two points are brought out: (*a*) unsaturation increases λ_0, bringing it nearer the visible region, as would be expected, and (*b*) with increasing molecular weight, λ_0 increases in the "vinyl" series and diminishes in the "ethyl" series.

R.	"Ethyl series." *	"Vinyl series."
Methyl	1610	2300
Ethyl	—	2380
n-Propyl	[1200] †	2400
n-Butyl	1530	2410
n-Amyl	1430	—

* Lowry, Pickard, and Kenyon, J., 1914, **105**, 94.
† Rotation too small to give trustworthy values.

The refractive indices of these four alcohols have been determined and a comparison of these with the values for the corresponding saturated alcohols shows clearly the exalting influence of

the double bond. A comparison of the densities shows that in each case the unsaturated alcohol has the greater density :—

	$D_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.		$D_{4^\circ}^{20^\circ}$.	
Methylvinylcarbinol	0·8320	1·4120	1·3954	0·8080	Methylethylcarbinol
Ethylvinylcarbinol	0·8406	1·4218	1·4094	0·8198	Ethylethylcarbinol
n-Propylvinylcarbinol	0·8370	1·4268	1·4141	0·8213	*n*-Propylethylcarbinol
n-Butylvinylcarbinol	0·8360	1·4337	1·4206	0·8227	*n*-Butylethylcarbinol

Several esters derived from two of these unsaturated alcohols and the *n*-fatty acids and benzoic acid have been prepared : their rotatory powers and other physical properties are given in the experimental part. As is the case with the aliphatic esters derived from the ethylalkylcarbinols, they have rotatory powers of opposite sign to that of the alcohol from which they are derived.

Specific Rotatory Powers in the Homogeneous State at 20°.

	$[\alpha]_D^{20^\circ}$.	
	Alcohol.	Acetate.
l-*n*-Butylvinylcarbinol	−25·0°	+ 4·36°
l-*n*-Butylethylcarbinol	− 8·13	+16·5

These data furnish additional support for the view expressed above—that in attempting to unravel the difficult problem of the relation between unsaturation and optical activity the compounds examined should be of the simplest possible chemical constitution.

All these esters exhibit complex rotatory dispersion; and so also do the esters derived from *n*-fatty acids and a large number of saturated aliphatic alcohols which have been described in previous parts of this series of communications. In order to explain why complex rotatory dispersion is exhibited by esters derived from alcohols which themselves show simple rotatory dispersion, advantage has been taken (J., 1914, **105**, 830) of the view put forward by Smedley (J., 1909, **95**, 931) that the carboxyl group can be represented by the two formulæ $-C\lessdot^{O}_{OH}$ and $-C\lessdot^{O}_{OH}$; the esters can thus be assumed to consist of equilibrium mixtures derived from the two forms of the carboxylic acid.

Recently Scheibler and Voss (*Ber.*, 1920, **53**, 388) have prepared potassio-derivatives of esters and they suggest the formulation of esters in such a manner that the presence of a mobile hydrogen atom is indicated; thus, for ethyl acetate

$$CH_3\cdot C\lessdot^{O}_{OEt} \rightleftharpoons CH_2{:}C\lessdot^{OH}_{OEt}$$

An alternative formulation of the isodynamic forms of these esters therefore appears available. This, however, is not the case, since

the formates derived from two of the above alcohols, as well as formates derived from methylethylcarbinol, methyl-*n*-hexylcarbinol and ethyl-*n*-hexylcarbinol (Part XIII, J., 1923, **123**, 1), exhibit complex rotatory dispersion. The formula of a formic ester does not permit the mobility of the hydrogen atom attached to the carbonyl group, unless the presence of bivalent carbon in the molecule is assumed; the suggestion of Scheibler and Voss cannot be considered in this connexion. A further proof of its inapplicability is to be found in the case of benzylmethylcarbinyl trimethylacetate,* which exhibits complex rotatory dispersion and yet does not possess a mobile hydrogen atom attached to the carbon atom immediately adjacent to the ester group.

EXPERIMENTAL.

Preparation of the Inactive Alcohols.—These alcohols, which have been very briefly described by Delaby (*loc. cit.*), were prepared by the interaction of acraldehyde † and the appropriate Grignard reagent, and were obtained in yields of 35—48%. The boiling points at the ordinary pressure were: Methylvinylcarbinol (after standing for several days over freshly ignited barium oxide), 96—98°; ethylvinylcarbinol, 113—114·5°; *n*-propylvinylcarbinol, 133—135°; *n*-butylvinylcarbinol, 153—155°.

The purity of each of the alcohols was determined by titration with a standard solution of bromine.

The hydrogen phthalic esters of the inactive alcohols were prepared by heating the alcohol with phthalic anhydride (in 10% excess) at 100° for 10 hours, and their purity was checked by titration with standard sodium hydroxide solution. Their properties are as follows:—

Melting Points.

	dl-.	*d*-.	*l*-.
Methylvinylcarbinyl hydrogen phthalate	+5°	52—53°	52—53°
Ethylvinylcarbinyl hydrogen phthalate	oil	oil	oil
n-Propylvinylcarbinyl hydrogen phthalate ...	‡62—63°	—	58—60°
n-Butylvinylcarbinyl hydrogen phthalate ...	56—57	50—52°	50—52

‡ Too soluble in all solvents for satisfactory crystallisation. The other solid esters were crystallised (generally in the form of prismatic needles) from ligroin.

Resolution of Methylvinylcarbinol.—Brucine (870 g.) was added to a warm solution of the hydrogen phthalate (400 g.) in

* Unpublished experiment.

† The acraldehyde was prepared by the excellent method of Moureu (*Ann. Chim.*, 1921, **15**, 158) and obtained in yields of about 65%. The product which distilled at 53·5—54·5° was stabilised by the addition of 0·5% of its weight of quinol.

acetone (2 litres), and the mixture heated until all the brucine had dissolved; the solution was then concentrated to half its bulk. The *brucine* salt, which separated on cooling in leaflets (m. p. 120—122°), was recrystallised seventeen times from acetone, when optical purity was reached. By the systematic working up of the mother-liquors, a further quantity of pure brucine salt was obtained, bringing the total to 140 g. The hydrogen phthalate obtained from this brucine salt crystallised from light petroleum in long, prismatic needles, m. p. 52—53°, $[\alpha]_D + 40{\cdot}5°$ ($c = 5$ in ethyl alcohol).

The partly active ($[\alpha]_D - 18°$) hydrogen phthalate obtained from the more soluble fractions of the brucine salt was combined with strychnine, morphine, quinine, cinchonine, cinchonidine, and quinidine, but none of these salts was obtained in the solid condition. The following procedure, however, gave the pure *l*-hydrogen phthalate. A sample of the ester ($[\alpha]_D - 18°$) was dissolved in warm ligroin with the addition of a few drops of ether; after a few days, a mixture of oil and crystalline material separated. The crystals had $[\alpha]_D - 30{\cdot}0°$ (in ethyl alcohol), and the oil $[\alpha]_D - 9°$ (in ethyl alcohol). After eight crystallisations from ligroin, the crystalline hydrogen phthalate reached constancy of melting point (52—53°) and of rotatory power ($[\alpha]_D - 40{\cdot}6°$ in ethyl alcohol). Both values are in excellent agreement with those of the corresponding *d*-isomeride.

Resolution of Ethylvinylcarbinol.—A solution of the hydrogen phthalic ester of ethylvinylcarbinol (457 g.) and finely-powdered strychnine (655 g.) in excess of absolute ethyl alcohol was concentrated until it was slightly syrupy, cooled, and kept over-night. The crystalline strychnine salt obtained (880 g. of m. p. 159—160°), after twelve recrystallisations, was optically pure. By systematic working up of the various filtrates, a total yield of 260 g. of optically pure strychnine salt was obtained: the hydrogen phthalate derived from the various crops had $[\alpha]_D + 26{\cdot}2°$ ($c = 5$ in ethyl alcohol). An attempt was made to resolve the hydrogen phthalate by crystallisation of the brucine salt from acetone, but although resolution did occur, it ceased when the specific rotatory power of the hydrogen phthalic ester derived from the least soluble crops of the brucine salt (m. p. 134—135°) reached $[\alpha]_D + 15{\cdot}5°$ ($c = 5$ in ethyl alcohol). All efforts to increase this value were fruitless, but it was subsequently found that a sample of hydrogen phthalate having $[\alpha]_D + 22{\cdot}0°$, when converted into brucine salt and crystallised from acetone until constancy of rotatory power was reached, had its rotatory power increased to $[\alpha]_D + 26{\cdot}3°$—a value almost identical with that exhibited by the ester obtained from the optically pure

strychnine salt. The hydrogen phthalate was obtained as a pale yellow, viscous oil which did not solidify on long standing.

Numerous unsuccessful attempts were made to obtain the optically pure *l*-hydrogen phthalate by fractional crystallisation of salts derived from other alkaloids; the salts were either not crystalline or too soluble for recrystallisation. Partially active hydrogen phthalate ($[\alpha]_D^{alc.}$ — 6·4°) was combined with benzidine (1 mol.), and the crystalline salt recrystallised several times from benzene. The least soluble fraction was the salt of the *dl*-ester, a microcrystalline powder, m. p. 96—98°.

The hydrogen succinate of ethylvinylcarbinol was therefore prepared (by heating the alcohol with succinic anhydride at 100° for 10 hours), and obtained as a viscous oil showing no tendency to crystallise. The salts of this ester with all the commoner alkaloids were obtained as very soluble gums. On heating the alcohol with diphenic anhydride, the hydrogen diphenate was obtained in crystalline needles, m. p. 55°. The alkaloidal salts of this ester also proved to be unsuitable for crystallisation.

Resolution of n-*Propylvinylcarbinol.*—Strychnine (448 g.) was dissolved in a hot solution of the hydrogen phthalate (325 g.) in absolute ethyl alcohol (1500 c.c.), and the whole concentrated to somewhat less than half its bulk. The *strychnine* salt separated in hard prisms, m. p. 164—166°, and sixteen recrystallisations were necessary before optical purity was reached. After a somewhat laborious working up of the mother-liquors, a total amount of 65 g. of pure strychnine salt, m. p. 170—172°, was obtained. The hydrogen phthalate obtained by the decomposition of this salt was a crystalline mass, m. p. 58—60°, which had $[\alpha]_D$ — 16·05° ($c = 5$ in ethyl alcohol).

The partly dextrorotatory hydrogen phthalate obtained from the more soluble fractions of the strychnine salt was converted into salts with numerous alkaloids, but, except in the case of brucine (see below), these were gums.

Crystallisation from light petroleum of the partly active hydrogen phthalic ester effected little or no separation. Although the hydrogen phthalate of the partly active alcohol is an oil, whilst that of the *dl*-alcohol is a solid of m. p. 62—63°, yet the latter is so excessively soluble in all solvents tried that it crystallises with extreme difficulty. In a similar manner, although the *p*-nitrobenzoate of the partially active alcohol is an oil whilst that of the *dl*-alcohol is a solid (leaflets, m. p. 60—62°), attempts to increase the rotatory power of the partially active ester by crystallisation were unsuccessful. In view of the failure to obtain the pure *d*-hydrogen phthalate, an attempt was made to prepare the

l-hydrogen phthalate by the use of another alkaloid as follows. Hydrogen phthalic ester having $[\alpha]_D$ — 12° was dissolved in acetone and mixed with a molecular quantity of brucine. The *brucine* salt separated in prismatic needles (m. p. 118—120°) which, after five recrystallisations from acetone, reached constancy of rotation. The hydrogen phthalate obtained from this salt had exactly the same rotatory power as that obtained from the strychnine salt.

Resolution of n-*Butylvinylcarbinol*.—A solution of strychnine (645 g.) and hydrogen phthalate (490 g.) in absolute ethyl alcohol (4,000 c.c.), on standing, deposited a crystalline crop of the *strychnine* salt. This resolution proceeded very smoothly and after eight recrystallisations constancy of rotatory power was reached. Altogether 250 g. of pure strychnine salt were obtained, in quadratic plates, m. p. 174—176°; these yielded a hydrogen phthalate, m. p. 50—52°, having $[\alpha]_D$ — 12·6° ($c = 5$ in ethyl alcohol). A sample of hydrogen phthalate (180 g.), having $[\alpha]_D$ — 9°, obtained from the more soluble fractions of the strychnine salt was combined with morphine (224 g.) in ethyl alcohol (500 c.c.). After cooling, the *morphine* salt separated (m. p. 112—114°) and after four recrystallisations was obtained with constancy of rotatory power. Altogether 120 g. of pure morphine salt were obtained in cubes, m. p. 114—116°. They gave, on decomposition, a hydrogen phthalate (m. p. 50—52°) having $[\alpha]_D$ + 12·6°.

Preparation of Esters.—The *formates* of *d*-ethylvinylcarbinol and of *d*-*n*-butylvinylcarbinol were prepared by heating the alcohols at 100° with a slight excess of anhydrous formic acid, the *acetates* of *d*-ethylvinylcarbinol and of *l*-*n*-butylvinylcarbinol and the n-*butyrate* of *d*-*n*-butylvinylcarbinol by the interaction of the alcohols and the requisite acid anhydride, and the *benzoate* of *d*-*n*-butylvinylcarbinol by the interaction of benzoyl chloride and the alcohol in pyridine solution. Each of the esters was redistilled until its refractive index was constant. The formate and the *n*-butyrate of *d*-*n*-butylvinylcarbinol were hydrolysed; the alcohol recovered in each case was of full rotatory power.

The b. p.'s (at 760 mm.) of the esters are as follows. Ethylvinylcarbinol: formate, 115·5—116·5°; acetate, 126·5—127·5°. *n*-Butylvinylcarbinol: formate, 155—157°; acetate, 165—167°; *n*-butyrate, 198—200°; benzoate, 152—153° (18 mm.).

Reduction of l-n-*Butylvinylcarbinol*.—The method first tried, in which platinum black was used as a catalyst (Vavon, *Ann. Chim.*, 1914, **1**, 144), was unsuccessful; the unsaturated alcohol was recovered unchanged after 48 hours' shaking in an atmosphere of hydrogen. Similarly, the hydrogen phthalate of the *l*-carbinol was recovered unchanged after prolonged shaking in an atmosphere of

Rotatory Powers of the Carbinols in the Homogeneous State at 20°.

Length of Observation Tubes—200 mm. for visual, 100 mm. for photographic readings.

λ.	*d*-Methylvinylcarbinol.		*d*-Ethylvinylcarbinol.		*l*-*n*-Propylvinylcarbinol.		*l*-*n*-Butylvinylcarbinol.	
Visual readings.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.
6708	+40·97°	25·00°	+43·69°	+25·98°	−35·60°	−21·22°	−32·36°	−19·31°
5893	55·67	33·89	59·16	35·20	48·52	28·92	43·94	26·20
5790	58·86	35·13	62·04	36·90	50·30	29·86	45·71	27·27
5461	67·17	40·38	71·36	42·44	57·62	34·55	52·85	31·53
4359	121·02	72·39	129·25	76·88	105·62	62·70	95·77	57·39
Photographic readings.								
4316	61·99	74·39	—	—	—	—	49·46	59·16
4272	—	—	—	—	56·38	67·20	50·88	60·81
4144	—	—	75	89·2	61·18	72·96	53·38	66·56
4077	72·99	87·46	—	—	64·18	76·54	59·18	70·06
4005	—	—	—	—	67·88	80·91	62·08	74·08
3979	78·49	94·13	—	—	69·18	82·44	62·88	74·92
3923	81·99	98·23	—	—	—	—	—	—
3830	—	—	95	113	—	—	—	—
$D^{20°}_{4°}$	0·8320		0·8406		0·8370		0·8360	

Rotatory Powers of the Esters in the Homogeneous State at 20°.

λ.	*d*-Ethylvinylcarbinyl formate. *l* = 25 mm.		*d*-Ethylvinylcarbinyl acetate. *l* = 50 mm.		*d*-*n*-Butylvinylcarbinyl formate. *l* = 100 mm.		*l*-*n*-Butylvinylcarbinyl acetate. *l* = 100 mm.		*d*-*n*-Butylvinylcarbinyl *n*-butyrate. *l* = 100 mm.		*d*-*n*-Butylvinylcarbinyl benzoate. *l* = 100 mm.	
	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.
6708	−5·94°	−26·59°	−3·61	− 8·48°	−12·25°	−13·99°	+2·74°	+3·16°	−1·83°	−2·11°	+30·41°	+30·30°
5893	7·75	34·69	4·78	11·14	15·61	17·83	3·78	4·36	2·50	2·88	41·60	41·47
5790	8·28	37·03	5·14	12·02	16·37	18·70	4·27	4·93	3·31	3·81	44·05	43·91
5461	9·43	42·17	5·90	13·82	20·18	23·05	4·54	5·23	3·47	3·99	51·43	51·26
4359	16·69	74·64	10·14	23·64	35·72	40·80	8·27	9·53	5·38	6·19	99·94	99·63
$D^{20°}_{4°}$	0·8953		0·8733		0·8754		0·8682		0·8696		1·0033	

Alcohols.

Observed rotations in a 50-mm. jacketed tube at different temperatures.

d-*Methylvinylcarbinol.*

$\lambda = 6708$	+ 10·40° at 21·2°; 9·35° at 38°; 8·08° at 58·5°; 7·40° at 80°
$\lambda = 5893$	13·80° at 21·2°; 12·54° at 38°; 10·81° at 59°; 9·26° at 75°.
$\lambda = 5790$	14·37° at 21·2°; 12·88° at 39°; 11·66° at 61°; 9·97° at 86°.
$\lambda = 5461$	16·51° at 21·2°; 14·92° at 39·5°; 13·33° at 61°; 10·77° at 86·5°.
$\lambda = 4359$	29·38° at 21·2°; 26·66° at 39°; 23·60° at 57°; 20·74° at 90·5°.

d-*Ethylvinylcarbinol.*

$\lambda = 6708$	+ 10·92° at 20°; 9·57° at 46°; 8·27° at 71°; 7·87° at 88°; 7·50° at 102°.
$\lambda = 5893$	14·79° at 20°; 12·86° at 48°; 11·80° at 68°; 10·74° at 88°; 10·23° at 100·5°.
$\lambda = 5790$	15·51° at 20°; 13·20° at 48·6°; 12·13° at 66·5°; 11·18° at 89°; 10·46° at 104°.
$\lambda = 5461$	17·84° at 20°; 15·36° at 48·3°; 14·04° at 67°; 12·83° at 89·5°; 12·22° at 103·8°.
$\lambda = 4359$	32·30° at 20°; 28·43° at 47·2°; 25·76° at 67°; 23·69° at 88·1°; 23·00° at 98·6°.

l-n-*Propylvinylcarbinol.*

$\lambda = 6708$	− 8·62° at 21·5°; 7·24° at 42°; 6·46° at 61°; 5·00° at 97°; 4·38° at 109°.
$\lambda = 5893$	11·56° at 21·5°; 9·16° at 43·5°; 8·90° at 64°; 6·44° at 97°; 6·16° at 109°.
$\lambda = 5790$	12·08° at 21·5°; 10·46° at 46·5°; 9·50° at 62°; 6·92° at 99°; 6·52° at 109°.
$\lambda = 5461$	14·03° at 21·5°; 11·86° at 47°; 10·82° at 63°; 8·06° at 99°; 7·50° at 109°.
$\lambda = 4359$	25·68° at 21·5°; 22·03° at 46°; 19·64° at 61·5°; 14·21° at 100°; 13·01° at 109°.

l-n-*Butylvinylcarbinol.*

$\lambda = 6708$	− 7·58° at 20·5°; 6·00° at 52°; 4·61° at 85°; 3·78° at 108°; 3·40° at 128°.
$\lambda = 5893$	10·27° at 20·5°; 8·94° at 53°; 6·10° at 85°; 5·16° at 108°; 4·36° at 130°.
$\lambda = 5790$	10·90° at 20·5°; 8·89° at 52°; 7·00° at 82·5°; 5·68° at 108°; 5·09° at 129°.
$\lambda = 5461$	12·65° at 20·5°; 10·20° at 52°; 8·01° at 82·5°; 6·51° at 109·5°; 5·85° at 128°.
$\lambda = 4359$	23·07° at 20·5°; 18·63° at 52·5°; 15·32° at 82·5°; 12·52° at 108°; 11·35° at 129°.

Ester.

d-*Ethylvinylcarbinyl acetate.*

$\lambda = 6708$	− 3·61° at 20°; 4·21° at 41°; 4·65° at 71°; 4·70° at 96°; 4·75° at 107°.
$\lambda = 5893$	4·78° at 20°; 5·45° at 44°; 5·72° at 72°; 5·90° at 98°; 5·95° at 107°.
$\lambda = 5790$	5·14° at 20°; 6·20° at 44°; 6·75° at 72°; 6·95° at 96°; 7·00° at 107°.
$\lambda = 5461$	5·90° at 20°; 7·10° at 42°; 7·82° at 71°; 7·91° at 97°; 7·96° at 105°.
$\lambda = 4359$	10·14° at 20°; 11·80° at 48°; 12·30° at 71°; 12·35° at 74°; 12·48° at 90°; 12·60° at 107°.

Specific Rotatory Powers of the Alcohols in Various Solvents.
Temperature 18—20°. $l = 200$ *mm.*

Alcohol.	Solvent.	Grams of solute in 100 c.c. of solution.	$[\alpha]_\lambda$. 6708.	5893.	5790.	5461.	4359.	4077.	4005.	3979.
			Visual.					Photographic.		
d-Ethylvinylcarbinol	Ethyl alcohol	5·125	+21·46°	+34·34°	+35·02°	+41·56°	+77·18°	—	—	—
,, ,,	Carbon disulphide	4·867	26·83	36·67	37·90	43·25	78·07	—	—	—
,, ,,	Benzene	5·1215	23·86	30·76	31·83	36·30	67·78	—	—	—
l-*n*-Butylvinylcarbinol	Ethyl alcohol	4·695	−18·50	−22·58	−24·50	−28·22	−50·61	—	—	—
,, ,,	Carbon disulphide	4·915	−18·46	−22·38	−22·79	−27·26	−50·05	—	—	—
,, ,,	*cyclo*Hexane	23·985	−19·83	−26·75	−28·06	−32·33	−58·70	−71·5	−75·5	−76·7

Refractive Indices, $n_\lambda^{20°}$.

	Carbinols of the formula $CH_2{:}CH{\cdot}CH(OH){\cdot}R$. R.				Esters. *d*-Ethylvinylcarbinyl		*n*-Butylvinylcarbinyl			
λ.	Me.	Et.	Pr.	Bu.	formate.	acetate.	formate.	acetate.	*n*-butyrate.	benzoate.
6708	1·4100	1·4192	1·4248	1·4310	1·4074	1·4080	1·4193	1·4164	1·4221	1·4990
6402	1·4103	1·4201	1·4251	1·4314	1·4079	1·4095	1·4199	1·4182	1·4225	1·4993
6096	1·4115	1·4209	1·4261	1·4324	1·4092	1·4108	1·4202	1·4191	1·4236	1·5004
5896	1·4120	1·4218	1·4268	1·4337	1·4104	1·4115	1·4225	1·4200	1·4241	1·5038
5882	1·4118	1·4223	1·4270	1·4334	1·4097	1·4112	1·4227	1·4198	1·4242	1·5038
5790	1·4126	1·4227	1·4283	1·4340	1·4102	1·4121	1·4229	1·4199	1·4243	1·5039
5782	1·4126	1·4226	1·4275	1·4339	1·4105	1·4121	1·4228	1·4203	1·4243	1·5039
5700	1·4128	1·4232	1·4278	1·4341	1·4109	1·4124	1·4231	1·4208	1·4245	1·5040
5461	1·4144	1·4245	1·4296	1·4361	1·4119	1·4137	1·4245	1·4232	1·4261	1·5081
5218	1·4157	1·4256	1·4305	1·4373	1·4134	1·4149	1·4249	1·4237	1·4270	1·5082
5153	1·4162	1·4264	1·4311	1·4377	1·4140	1·4153	1·4253	1·4239	1·4273	1·5091
5106	1·4165	1·4265	1·4315	1·4378	1·4144	1·4156	1·4257	1·4241	1·4272	1·5097
4359	1·4235	1·4339	1·4339	1·4457	1·4208	1·4222	1·4340	1·4355	1·4263	1·5253

Densities.

All determinations of density were carried out with a pyknometer of about 1·5 c.c. capacity.

d-Methylvinylcarbinol. $D^{t°}_{4°}$ 0·8362 at 15·5°, 0·8156 at 39°, 0·7979 at 59·5°, 0·7746 at 84°.

d-Ethylvinylcarbinol. 0·8404 at 20·5°, 0·8200 at 42·8°, 0·8021 at 60·8°, 0·7890 at 76·2°, 0·7764 at 88·2°.

l-n-Propylvinylcarbinol. 0·8403 at 15°, 0·8186 at 42°, 0·7928 at 68·5°, 0·7656 at 94°, 0·7432 at 120°.

d-n-Butylvinylcarbinol. 0·8345 at 22·8°, 0·8144 at 49°, 0·7918 at 73·5°, 0·7628 at 110°, 0·7528 at 121°.

d-Ethylvinylcarbinyl formate. 0·8902 at 25·5°, 0·8699 at 46·5°, 0·8514 at 65°, 0·8242 at 94°, 0·8157 at 102°.

d-Ethylvinylcarbinyl acetate. 0·8805 at 22·1°, 0·8626 at 31·6°, 0·8521 at 54°, 0·8291 at 73·5°, 0·8085 at 88°, 0·7975 at 100·5°.

	$D^{20°}_{4°}$.
d-n-Butylvinylcarbinyl formate	0·8754
" " " acetate	0·8682
" " " *n*-butyrate	0·8696
" " " benzoate	1·0033

hydrogen. The second method, due to Skita (*Ber.*, 1912, **45**, 3589), was completely successful; the calculated quantity of hydrogen was absorbed within 2½ hours. After the physical constants of the *l*-butylethylcarbinol had been determined, the alcohol was converted into its hydrogen phthalate by the ordinary method and the constants of this crystalline compound were determined. Thus the identity of the reduced alcohol was completely established. In a further experiment *l-n*-butylvinylcarbinyl acetate, which had $[\alpha]_D + 4·36°$, was reduced by Skita's method; on account of the difficulty of isolating the reduced ester without some hydrolysis taking place (owing to acetic acid being used as solvent), its complete hydrolysis was effected, and the product isolated as the reduced alcohol, the rotatory power of which was identical with that of the alcohol obtained by the reduction of the unsaturated alcohol.

Some of the materials used in this investigation were purchased with the aid of a grant from the Government Grant Committee of the Royal Society, to whom the authors express their thanks. One of the authors (D. R. S.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance allowance which enabled him to participate in the work.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, March 17th*, 1925.]

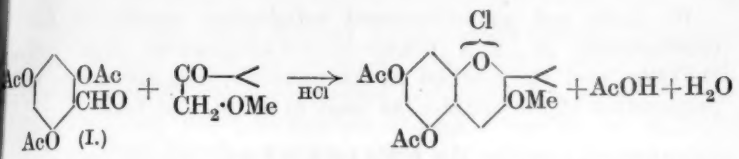
CLXIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part VII. The Preparation of the Anthocyanidins with the Aid of 2:4:6-Triacetoxybenzaldehyde.*

By DAVID DOIG PRATT and ROBERT ROBINSON.

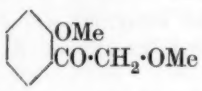
HAVING completed the task of the synthesis of the three fundamental anthocyanidins and of the pyrylium salts most closely related to the more important naturally occurring flavones and flavonols, we have turned our attention to improvements of method especially such as would render feasible the synthesis of the methyl ethers of cyanidin and delphinidin, *e.g.*, peonidin, oenidin, or myrtillidin. Demethylation with hydriodic acid, employed as the final stage in every previous case, is obviously inadmissible and either the hydroxyl and methoxyl groups must be present in the components as such in the desired positions, or the former must be protected by groups, such as acetyl or carbomethoxy, which can be readily removed by acid hydrolysis under moderate conditions. Since most of the natural methylated anthocyanidins contain hydroxyl groups in positions 5 and 7 in the phloroglucinol nucleus, it was of primary importance to devise a method whereby phloroglucinaldehyde could be employed in syntheses of the type which we are developing. Owing to the high reactivity displayed by this substance and its great tendency to pass into red insoluble products in presence of mineral acid our experience of the direct process was most discouraging. If, however, the nuclear reactivity of the aldehyde is depressed by acetylating all the hydroxyl groups and the condensations are carried out in absolute formic * acid solution, satisfactory results are obtained and the method constitutes by far the most convenient process for the preparation of the anthocyanidins.

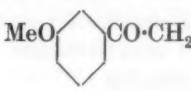
2:4:6-*Triacetoxybenzaldehyde* (I) reacts with ω-methoxyacetophenone derivatives in presence of hydrogen chloride in accordance with the scheme:

* The use of 80% formic acid as a solvent in condensations to pyrylium salts was introduced by Buck and Heilbron (J., 1922, **121**, 1199) and in our experience tends to increase yields. The very numerous syntheses of this class described as occurring in acetic acid solution would no doubt in the majority of cases proceed more satisfactorily in the new medium. In the reactions described in this communication we employ absolute formic acid in order to avoid premature hydrolysis of the acetyl groups, and the first appearance of intense colour after the introduction of hydrogen chloride usually synchronises with the evolution of carbon monoxide.

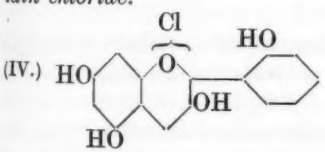


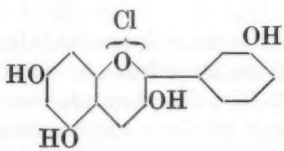
The salt precipitated from the reaction mixture by ether is hydrolysed by boiling aqueous alcoholic hydrochloric acid. In this way, using the ketonic components previously coupled with 2-hydroxy-4 : 6-dimethoxybenzaldehyde, we have prepared pelargonidin chloride 3 : 4′-dimethyl ether, cyanidin chloride 3 : 3′ : 4′-trimethyl ether, morinidin chloride 3 : 2′ : 4′-trimethyl ether, and delphinidin chloride 3 : 3′ : 4′ : 5′-tetramethyl ether. On demethylation of these salts by the usual series of processes pelargonidin, cyanidin, morinidin and delphinidin salts, respectively, were obtained. Two new isomerides of pelargonidin have been synthesised. *o*-Methoxybenzoyl chloride and *m*-methoxybenzoyl chloride react with ethyl sodio-αγ-dimethoxyacetoacetate in ethereal solution to give products which yield ω : 2-dimethoxyacetophenone (II) and ω : 3-dimethoxyacetophenone (III), respectively, on hydrolysis. These ketones yield, on condensation with 2 : 4 : 6-





triacetoxybenzaldehyde, hydrolysis, and demethylation of the products, 3 : 5 : 7 : 2′-tetrahydroxyflavylium chloride (IV) and 3 : 5 : 7 : 3′-tetrahydroxyflavylium chloride (V). The former is related to the flavonol datiscetin and is therefore termed *datiscetinidin chloride*.



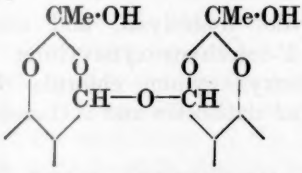


It is of interest to compare the behaviour of these salts with that of pelargonidin chloride. The details of the colour reactions will be found in the experimental section, but a striking experiment may be mentioned here. An alcoholic solution of each salt is diluted with much water. The colour base of datiscetinidin is at once precipitated, the solution of (V) is decolorised, owing to pseudo-base formation, in a very short time, whilst the pelargonidin solution remains clear and dark brownish-red. In time, the pelargonidin solution also deposits some colour-base and pseudo-base remains in solution.

We have not yet discovered satisfactory conditions for the condensation of 2 : 4 : 6-triacetoxybenzaldehyde with ketones R·COMe, and the method is, for example, not applicable to the preparation of luteolinidin, at least in its present form.

EXPERIMENTAL.

2 : 4 : 6-*Triacetoxybenzaldehyde* (I).—Acetic anhydride (50 c.c.) was added to a mixture of phloroglucinaldehyde (10 g.) and potassium carbonate (10 g.), when considerable heat was evolved, and on subsidence of the reaction a further portion of potassium carbonate (5 g.) was introduced. The mass was well stirred and after an hour water was added and the precipitate collected, washed, drained, and heated to boiling with methyl alcohol (50 c.c.). The derivative, which separated in prisms on cooling, was washed with a little methyl alcohol and dried in air (yield 12·5—14 g.). This product is almost pure and can be employed for most purposes. The substance crystallises from methyl alcohol in colourless, hexagonal prisms, m. p. 151° (Found, in material dried in a vacuum over sulphuric acid: C, 54·0; H, 4·6; in material dried at 100°: C, 54·1; H, 4·6. $C_{13}H_{12}O_7,0{\cdot}5H_2O$ requires C, 54·0; H, 4·5%). Prolonged heating above 100° causes some decomposition and we have no evidence regarding the mode of combination of the attached water. This may well be constitutional and some such arrangement as the following is possible:



The substance is insoluble in cold dilute aqueous sodium hydroxide and gives no coloration with ferric chloride in alcoholic solution.

ω : 2-*Dimethoxyacetophenone* (II).—Ethyl αγ-dimethoxyacetoacetate * (29·5 g.) was converted into its sodio-derivative by means of granulated sodium (3·6 g.) in ethereal suspension, and *o*-methoxybenzoyl chloride (25·5 g.) then added to the mixture which, after subsidence of the initial gentle reaction, was heated on the steam-bath under reflux for 4 hours. The neutral product was isolated (42 g.) and hydrolysed by aqueous potassium hydroxide (900 c.c. of 2·5%), first in the cold by agitation for 12 hours and then at the boiling point for 4 hours. The cooled liquid was saturated with potassium carbonate and extracted with ether. The ketone (12 g.),

* The proportion of sodium, used in the preparation of this substance from ethyl methoxyacetate, previously suggested (this vol., p. 168) can advantageously be increased by 50%.

b. p. 165°/15 mm., was isolated in the usual manner (Found: C, 66·7; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). The oil could not be induced to crystallise and yielded a *semicarbazone* crystallising from water in clusters of jagged needles, m. p. 137°.

In an entirely similar manner, ethyl αγ-dimethoxyacetoacetate (36 g.) and *m*-methoxybenzoyl chloride (32 g.) gave rise to 12·5 g. of a pale yellow oil consisting of ω : 3-*dimethoxyacetophenone* (III), b. p. 155°/18 mm. (Found: C, 66·8; H, 6·6%). The *semicarbazone* crystallises from aqueous alcohol in clusters of colourless needles, m. p. 128°.

Datiscetinidin Chloride 3 : 2′-*Dimethyl Ether* (corresponding with IV).—Hydrogen chloride was passed for 2 hours through a mixture of ω : 2-dimethoxyacetophenone (3·1 g.), 2 : 4 : 6-triacetoxybenzaldehyde (5 g.), and formic acid (15 c.c.). After 12 hours, a considerable crystallisation of a bright red substance had occurred and after the addition of a large volume of ether the solid was collected and added to ethyl alcohol (500 c.c.) containing concentrated hydrochloric acid (10 c.c.). On boiling, the salt did not pass completely into solution. The mixture was heated under reflux for 1·5 hours, concentrated hydrochloric acid (40 c.c.) added, and the alcohol removed as far as possible by distillation from the steam-bath. Water was added and the solid collected and washed with 0·5% hydrochloric acid. The well-drained material was added to boiling water (750 c.c.) and hydrochloric acid (10 c.c. of 10%) and precipitated from the filtered solution in slender, orange-red needles (3 g.) by the addition of 20% hydrochloric acid (100 c.c.) (Found, in material dried in a vacuum: C, 60·6; H, 4·5. $C_{17}H_{15}O_5Cl$ requires C, 60·9; H, 4·5%). This salt is characterised by its extremely sparing solubility even in hot dilute hydrochloric acid and by its orange-red colour. It darkens at 250°, but does not melt at 280°.

Datiscetinidin Chloride (IV).—A mixture of dimethyldatiscetinidin chloride (2 g.), phenol (6 g.), and hydriodic acid (50 c.c.; *d* 1·7) was gently boiled in a stream of carbon dioxide for 30 minutes; on cooling, the demethylated iodide crystallised in slender, red needles. These (1 g.) were dissolved in alcohol (20 c.c.) containing a trace of hydrogen chloride and an excess of silver chloride, and the mixture was heated gently for 15 minutes. Hydrochloric acid (20 c.c. of 12%) was added to the filtered solution, and the chloride then separated in fine, red needles which darkened at 240° (Found, in material dried in a vacuum over sulphuric acid: C, 55·3; H, 4·3. $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·5; H, 4·0%). This salt is very sparingly soluble in dilute hydrochloric acid, and the colour of its solutions in the simple alcohols is red, bluer than that of galanginidin but not so blue nor so intensely coloured as a solution of pelar-

gonidin of similar concentration. In alcoholic solution, a trace of sodium carbonate gives a violet coloration, which, on the addition of more sodium carbonate, becomes at once more intense and duller in tone, whilst on dilution with water the colour is reddish-violet. The reactions are the same when sodium hydroxide is employed. The formation of pseudo-base and of colour-base was observed, but, as in the case of morinidin, the former appears to undergo further change in solution.

5 : 7-*Dihydroxy*-3 : 3′-*dimethoxyflavylium Chloride* (corresponding with V).—The condensation of ω : 3-dimethoxyacetophenone (6·2 g.) with 2 : 4 : 6-triacetoxybenzaldehyde (10 g.) in formic acid (40 c.c.) solution by means of hydrogen chloride was carried out in 3 hours. The product, precipitated by ether, was dissolved in alcohol (300 c.c.), to which concentrated hydrochloric acid (50 c.c.) was later added. The solution was boiled for 15 minutes and the alcohol removed by distillation from the steam-bath and finally by evaporation in a vacuum. The crystalline precipitate was washed with 0·5% hydrochloric acid, dissolved in 400 c.c. of hot 0·5% hydrochloric acid, and the solution filtered. The addition of 10% hydrochloric acid (200 c.c.) caused deep brownish-crimson clusters of microscopic needles to separate, even from the hot solution. Further quantities could be obtained from the original mother-liquor and from the residue, and the total yield was 6·8 g. (Found, in material dried in a vacuum over sulphuric acid: C, 57·9; H, 5·0. $C_{17}H_{15}O_5Cl,H_2O$ requires C, 57·8; H, 4·8%).

The salt darkens at 195° and decomposes at 225°. The substance is much more readily soluble in alcohol than the isomerides described in this communication, and when the cherry-red solution is largely diluted with water complete decoloration is rapid. The orange-red colour of the oxonium salt is quantitatively restored by the addition of hydrochloric acid.

3 : 5 : 7 : 3′-*Tetrahydroxyflavylium Chloride* (V).—The salt last described (3 g.) was demethylated by boiling hydriodic acid (80 c.c.; *d* 1·7) in presence of phenol (15 g.) during 30 minutes. After cooling, the red, prismatic needles were collected (1·8 g.) and washed with ether. Conversion into the chloride was carried out in ethyl alcohol (30 c.c.) and the filtered solution was mixed with hydrochloric acid (30 c.c. of 6%). The chloride separated in prismatic needles and was recrystallised from hot 6% hydrochloric acid (Found, in material dried in a vacuum over sulphuric acid: C, 55·8; H, 4·2. $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·5; H, 4·0%). The salt decomposes at 200°. Its acid alcoholic solutions resemble those of pelargonidin, but the tone is duller and browner. The substance is more soluble in dilute hydrochloric acid than datiscetinidin or pelargonidin

chloride and it is distinguished from its isomerides by a remarkable faculty for passing into the pseudo-base. Aqueous alkaline solutions are reddish-violet, whilst in alcoholic solution a curiously dichroic reddish-blue colour is produced by addition of a trace of sodium hydroxide or excess of sodium carbonate. A trace of sodium carbonate gives a violet solution. This salt and also datiscetinidin chloride, like pelargonidin chloride, reduces Fehling's solution and is extracted from aqueous solution by *iso*amyl alcohol.

Pelargonidin Chloride 3 : 3′-Dimethyl Ether.—Hydrogen chloride was led for 2 hours through a solution of ω : 4-dimethoxyacetophenone (5·4 g.) and 2 : 4 : 6-triacetoxybenzaldehyde (8 g.) in absolute formic acid (25 c.c.). The deep crimson product was precipitated by the addition of much ether and dissolved as far as possible in boiling ethyl alcohol, to which concentrated hydrochloric acid (50 c.c.) was added. The mixture was boiled for 10 minutes, diluted with an equal volume of water, and, after cooling, the solid was collected. The oxonium salt was then isolated by extraction with boiling water containing a little hydrochloric acid (about 0·1%). On addition of concentrated hydrochloric acid to the filtrates, the very sparingly soluble dimethylpelargonidin chloride separated completely, and to a large extent from the hot liquid, in intense crimson rosettes and sheaves of glistening, microscopic needles (6·5 g.). The salt was recrystallised from 0·5% hydrochloric acid (Found, in material dried in a vacuum : C, 61·1; H, 4·8. $C_{17}H_{15}O_5Cl$ requires C, 60·9; H, 4·5%). The substance also crystallises in squat prisms; it does not melt at 300°. Its orange solution in sulphuric acid exhibits a green fluorescence. The colour of an acid alcoholic solution resembles that of pelargonidin, but is rather less bluish-red in tinge. When the crystals are covered with distilled water, a portion dissolves to a pinkish-yellow solution which very soon becomes colourless. On heating with distilled water a deep orange solution is obtained and this also becomes colourless on great dilution. Also the orange solution treated with sodium acetate gives a dull brownish-violet colour-base which rapidly passes into colourless solution. All these decolorised solutions contain the pseudo-base and become orange on the addition of hydrochloric acid. On shaking an aqueous solution with *iso*amyl alcohol, the colour passes completely to the latter. The intense cherry-red extract with aqueous sodium carbonate gives a yellow watery layer and a pale purplish-brown alcoholic layer.

Pelargonidin Chloride.—Demethylation of the dimethyl ether (3 g.) was carried out during 30 minutes by means of a gently boiling mixture of hydriodic acid (100 c.c.; *d* 1·7) and phenol (10 g.). On cooling, the iodide (3·1 g.) separated in glistening, rectangular

prisms. The supposed pelargonidin chloride obtained from this persisted in crystallising in highly characteristic, diamond-shaped plates, and as pelargonidin chloride has never been observed to separate in this form we concluded that the specimen was contaminated with methylated material; the sodium carbonate reaction was also purple rather than blue. The substance was therefore again demethylated, relatively twice as much phenol being used. The recovered iodide was converted into chloride and this was identical in every respect with pelargonidin chloride. The colour of acid solutions, the form of the crystals obtained under different conditions of crystallisation, the blue colour in sodium carbonate solution, the colour-base, the formation of pseudo-base, and the chief absorption band in alcoholic solution were examined.

Morinidin Chloride 3 : 2′ : 4′-*Trimethyl Ether*.—A solution of ω : 2 : 4-trimethoxyacetophenone (5 g.) and 2 : 4 : 6-triacetoxybenzaldehyde (7 g.) in formic acid (25 c.c.) was saturated with hydrogen chloride during 3 hours, and ether added to the dark red solution until no further precipitation occurred. The viscous material insoluble in ether was well washed with the solvent and dissolved in ethyl alcohol (50 c.c.), and concentrated hydrochloric acid (30 c.c.) added. On boiling, the anthocyanindin-like colour became much intensified and in a few minutes the whole of the salt crystallised from the hot solution. The substance was crystallised from boiling methyl alcohol by the addition of hydrochloric acid to the filtered solution. It separated in brick-red, short, microscopic needles and in a similar form from hot very dilute hydrochloric acid (about 0·5%) (Found, in material dried in a vacuum over sulphuric acid: C, 59·4; H, 4·9. $C_{18}H_{17}O_6Cl$ requires C, 59·3; H, 4·7%). The salt gradually darkens on heating at 250°, but does not melt at 300°. Aqueous solutions of this salt are orange-red; on dilution a crimson colour is obtained and on great dilution, decoloration ensues. The orange colour is restored by the addition of a mineral acid. The colour-base is a dark mauve-crimson precipitate and the solution in aqueous ammonia is blood-red. The red solution in sulphuric acid has a bright green fluorescence. The dry chloride is insoluble in chloroform, but on the addition of a trace of ferric chloride an eosine-red solution is at once produced. The *perchlorate* is extremely sparingly soluble in dilute aqueous perchloric acid and crystallises from alcohol containing a little perchloric acid in slender, microscopic, crimson needles. The trimethylmorinidin chloride (1·8 g.) was mixed with phenol (5 g.) and hydriodic acid (50 c.c.; *d* 1·7), and the mixture boiled for 25 minutes in a neutral atmosphere. On cooling, the iodide separated in hair-fine, red needles (1·8 g.). The related chloride showed all the properties

of morinidin chloride as previously described (this vol., p. 1137; compare Willstätter and Schmidt, *Ber.*, 1924, **57**, 1945). The addition of hydrogen peroxide to the dichroic solution of morinidin chloride in aqueous sodium carbonate gives a brownish-yellow, intensely green, fluorescent solution, but definite products have not yet been isolated from this.

Cyanidin Chloride 3 : 3′ : 4′-*Trimethyl Ether*.—The quantities, times, and method employed in preparing this salt from ω-methoxyacetoveratrone (this vol., p. 170) were the same as those given above in the case of trimethylmorinidin. The hydrolysis of the product was conducted at the boiling point for 15 minutes. The paste obtained on cooling was transferred to the filter with the aid of alcohol (15 c.c.), mixed with concentrated hydrochloric acid (15 c.c.), well drained, and dried (7 g.). The substance was dissolved in hot ethyl alcohol (160 c.c.), and concentrated hydrochloric acid (10 c.c.) added to the filtered solution. The deep crimson solution deposited dense aggregates of small needles (Found, in material dried in a vacuum over sulphuric acid: C, 55·2; H, 5·3. $C_{18}H_{17}O_6Cl,1{\cdot}5H_2O$ requires C, 55·2; H, 5·1%). This specimen decomposed at 208°. The properties of this salt closely resemble those of dimethylpelargonidin chloride. The red alcoholic solution has a slightly more bluish shade and the salt is more readily soluble in dilute hydrochloric acid. In time, it separates completely from 0·5% hydrochloric acid solution.

Cyanidin Chloride.—A mixture of trimethylcyanidin chloride (3 g.), phenol (6 g.), and hydriodic acid (150 c.c.; *d* 1·7) was heated to gentle ebullition for 35 minutes in a stream of carbon dioxide. Reddish-brown, prismatic needles separated from the hot solution and, on cooling, the substance was collected, washed with ether, and dried (3 g.). The iodide exhibits a golden lustre and does not melt at 300°. The chloride obtained by double decomposition with silver chloride in the usual manner exhibited the characteristic reactions of cyanidin and was found by careful direct comparison to be identical with the specimen of the anthocyanidin previously synthesised (this vol., p. 172), which had itself been compared with an authentic specimen of natural origin.

Delphinidin Chloride 3 : 3′ : 4′ : 5′-*Tetramethyl Ether*.—Hydrogen chloride was passed through a solution of ω : 3 : 4 : 5-tetramethoxyacetophenone (2·8 g.) (this vol., p. 173) and 2 : 4 : 6-triacetoxybenzaldehyde (3·6 g.) in formic acid (15 c.c.) for 2·5 hours. On the addition of ether the syrupy residue gradually crystallised, the mass exhibiting brown-golden reflex. The washed product dissolved completely in ethyl alcohol (30 c.c.) and after the addition of concentrated hydrochloric acid (15 c.c.) the mixture was boiled

for 20 minutes and cooled. The crystals (1·8 g.) were recrystallised by very slow cooling of a hot solution of the whole in 6% aqueous hydrochloric acid (1200 c.c.). The slender, glistening needles exhibit a dark green reflex and do not melt at 250° (Found, in material dried in a vacuum: C, 53·2; H, 5·6. $C_{19}H_{19}O_7Cl,2H_2O$ requires C, 53·0; H, 5·3%). This substance dissolves in alcohol to a blue cherry-red solution which is rapidly decolorised on dilution with water, the colour being fully restored by addition of mineral acid. Although containing four methoxyl groups, the substance in solution in aqueous sodium carbonate has a greenish-brown tinge, and its solutions do not resemble those of the anthocyanidins. This salt, like all the other 5 : 7-dihydroxyflavylium chlorides here described, is sparingly soluble in dilute hydrochloric acid and exhibits a strong tendency to crystallise.

Delphinidin Chloride.—A mixture of the tetramethyl ether (1 g.), phenol (5 g.), and hydriodic acid (50 c.c.; *d* 1·7) was boiled in an atmosphere of carbon dioxide for 30 minutes. The iodide crystallised, on cooling, in prismatic needles with a golden-green reflex and was isolated (1 g.). After conversion to the chloride, the identity of the salt with delphinidin chloride was established by comparison with the specimen previously synthesised (this vol., p. 174) in respect of the colour in acid solutions, formation of colour-base and pseudo-base, solubility of the salts in 5% hydrochloric acid and 7% sulphuric acid, the ferric chloride reaction in alcohol and in water, and the colours of the solutions in aqueous sodium carbonate. The appearance of the crystals in mass and under the microscope was identical in both cases, and the characteristic hydrate, $C_{15}H_{11}O_7Cl,2H_2O$, was obtained in flat prisms, sparingly soluble in 5% hydrochloric acid and 7% sulphuric acid.

One of us (D. D. P.) desires to express his thanks to the Carnegie Trust for a Fellowship which has enabled him to take part in this investigation.

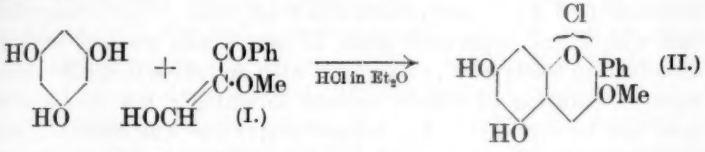
THE UNIVERSITY, MANCHESTER. [*Received, March 17th,* 1925.]

CLXIV.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part VIII. A New Synthesis of Pelargonidin Chloride and of Galanginidin Chloride.*

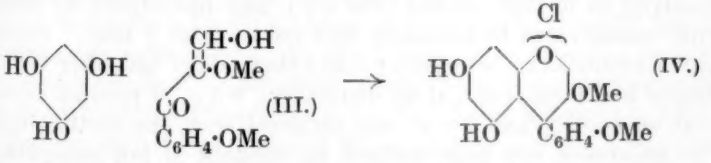
By THOMAS MALKIN and ROBERT ROBINSON.

Two of the three chief methods available for the preparation of hydroxybenzopyrylium salts having been exploited by Willstätter and his colleagues and by Pratt and Robinson in the synthesis of

the anthocyanidins, we have directed our attention to the third process, that of C. Bülow, in order to determine whether it also is available for this purpose. The first case chosen was that of galanginidin (Willstätter and Schmidt, *Ber.*, 1924, **57**, 1945; Pratt and Robinson, this vol., p. 1135), the 3-methyl ether (II) of which we have prepared by the 2 : 4 : 6-triacetoxybenzaldehyde method (preceding paper) for comparison with the salt obtained according to the scheme :



The two substances were identical and the methyl ether was converted into galanginidin chloride by the usual series of processes. The hydroxymethylene derivative (I) of ω-methoxyacetophenone is a crystalline enolic substance obtained without difficulty as its sodium salt by condensation of the ketone with ethyl formate in presence of sodium ethoxide. When ω : 4-dimethoxyacetophenone was condensed with ethyl formate in a similar manner, an oily hydroxymethylene derivative was produced, and this was condensed with phloroglucinol by means of hydrogen chloride to a pelargonidin chloride dimethyl ether, which was very similar to the substance obtained by Pratt and Robinson (preceding paper) from 2 : 4 : 6-triacetoxybenzaldehyde and ω : 4-dimethoxyacetophenone, but crystallised with $1H_2O$ under conditions whereby the latter salt is obtained anhydrous. We saw little sign of heterogeneity of our new product, but have reason to suspect that the substance obtained as described in this communication is mixed with some *epi*pelargonidin dimethyl ether (IV), which might arise in the following manner :



On demethylation and conversion into chloride, a substance was obtained which had the composition and chief properties of pelargonidin chloride, but from which only a small amount of pure pelargonidin chloride of undoubted authenticity could be isolated. The purification was necessarily wasteful and we have no suggestion to offer in regard to the relative amounts of true pelargonidin and pelargonidin-like impurity which were present in the mixture.

We conclude that, on account of the possibility that mixtures may be obtained, the Bülow method is likely to prove an inferior procedure in the synthesis of anthocyanidins.

EXPERIMENTAL.

Phenyl α-Methoxy-β-hydroxyvinyl Ketone (I).—A mixture of ω-methoxyacetophenone (10 g.) and ethyl formate (6 g.) was gradually added with cooling in melting ice to a suspension of sodium ethoxide (4·5 g.) in anhydrous ether (25 c.c.). The orange sodium salt which had separated after 12 hours was washed with ether, dissolved in water at 0°, and mixed with an excess of a cold saturated aqueous solution of copper acetate to which a few drops of acetic acid had been added. The copper derivative was collected, washed with water and ether, and dried. A further quantity could be recovered by shaking the ethereal filtrate from the sodium salt with aqueous copper acetate, thus bringing the total yield to 6 g. The substance could not be recrystallised, but a good specimen melted at 178° (Found: C, 57·4; H, 4·6. $C_{20}H_{18}O_6Cu$ requires C, 57·5; H, 4·3%). When this copper salt (4 g.) was decomposed with 5% sulphuric acid in presence of ether, and the ethereal solution was washed with water and evaporated to a small bulk, the free hydroxymethylene ketone (3 g.) separated in the crystalline condition. The substance crystallises from ether in almost colourless, elongated prisms, m. p. 112° (Found: C, 67·4; H, 5·5. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). In alcoholic solution, the compound gives a brownish-purple coloration with ferric chloride.

Galanginidin Chloride 3-Methyl Ether (II).—(A). Hydrogen chloride was passed for 3 hours through a solution of 2 : 4 : 6-triacetoxybenzaldehyde (11·6 g.) and ω-methoxyacetophenone (6 g.) in absolute formic acid (30 c.c.). After 12 hours, the oxonium salt was precipitated by the addition of much ether, collected, dissolved in methyl alcohol (480 c.c.), and hydrolysed by boiling with concentrated hydrochloric acid (30 c.c.) for ½ hour. Concentrated hydrochloric acid (90 c.c.) was then added and, after half the alcohol had been removed by distillation, 6·5 g. of product crystallised on cooling and 1·0 g. was obtained from the mother-liquor. The substance was recrystallised by solution in hot hydrochloric acid (less than 0·5%), sufficient concentrated acid being added to the filtered liquid to bring the concentration to 5% (Found, in material dried in a vacuum over sulphuric acid: C, 59·5; H, 4·8. $C_{16}H_{13}O_4Cl,H_2O$ requires C, 59·5; H, 4·7%).

(B). Hydrogen chloride was led for 1 hour through a solution of phenyl α-methoxy-β-hydroxyvinyl ketone (0·7 g.) and phloroglucinol (0·49 g.) in dry ether (25 c.c.). After a few hours the dark crimson

crystalline precipitate was collected (0·7 g.) and crystallised as under (A) (Found: C, 59·5; H, 4·6%). Careful comparison showed that the substances obtained by these two methods are identical. In mass the substance is brownish-crimson, but the elongated, almost rectangular plates are deep orange-brown by transmitted light. Both specimens crystallised (under conditions which could not be definitely ascertained) in curved, frond-like aggregates. The salt is sparingly soluble in cold water and, on boiling, an orange solution containing much pseudo-base is obtained. In dilute hydrochloric acid, the salt is very sparingly soluble and on great dilution, decoloration occurs, the colour being restored by the addition of acid. Amyl alcohol extracts the salt completely from aqueous solution, and the colour of the red alcoholic solution is almost completely discharged on the addition of sodium carbonate. The tendency of the substance to form pseudo-base in neutral or alkaline solution is very marked. On the addition of sodium acetate to an acid solution a deep mauve precipitate of colour base is obtained, but on dilution this dissolves to a colourless solution. The *perchlorate* was prepared from specimens made by methods (A) and (B) and identical results were obtained. The derivative is thrown down from aqueous solutions in long, fine needles. It crystallises from glacial acetic acid (0·1 g. in 15 c.c.) in deep brown, flat, elongated, rectangular prisms having a golden reflex. It does not melt below 300°, but chars slightly at 255—260°.

Galanginidin Chloride.—This salt can best be obtained by demethylation of its 3-methyl ether prepared by method (A) above. The chloride (4 g.), phenol (24 g.), and hydriodic acid (100 c.c.; *d* 1·7) were heated at 150° in a stream of carbon dioxide for 35 minutes. On cooling, 1·0 g. of iodide crystallised, and a further 1·5 g. was obtained after mixing the filtrate with an equal volume of ether. The conversion to chloride was carried out by heating in methyl alcohol (50 c.c.) with precipitated silver chloride (5 g.) on the steam-bath for 20 minutes, and, on the addition of hot 5% hydrochloric acid (70 c.c.) to the filtrate, crystallisation of 1·5 g. occurred immediately. Elongated prisms were obtained by recrystallisation from 3·5% hydrochloric acid, 1·2 g. being dissolved in 300 c.c. of boiling, very dilute acid and 25 c.c. of concentrated acid added. (Found, in material dried to constant weight in a vacuum over sulphuric acid: C, 60·5; H, 4·2. $C_{15}H_{11}O_4Cl,0{\cdot}5H_2O$ requires C, 60·1; H, 4·0%). The substance exhibited the reactions described by Willstätter and Schmidt (*loc. cit.*) and by Pratt and Robinson (*loc. cit.*). The former authors describe large, air-dried prisms containing $4H_2O$, and microscopic crystals, containing $2H_2O$, which lost $1H_2O$ in a vacuum desiccator. Pratt and Robinson found

$2H_2O$ after short drying in a desiccator. These observations are not necessarily inconsistent. The reactions of the salt were similar to those previously recorded.

Anisyl α-Methoxy-β-hydroxyvinyl Ketone (III).—A solution of ω : 4-dimethoxyacetophenone (10 g.) and ethyl formate (4·8 g.) in anhydrous ether (30 c.c.) was slowly added to a suspension of sodium ethoxide (3·8 g.) in ether (30 c.c.), cooled in melting ice. The sodium salt of the hydroxymethylene derivative slowly separated from the red solution and after several hours the mixture was agitated with an equal volume of ice-cold water and the separated aqueous layer treated with a saturated solution of copper acetate. The precipitated salt was washed and dried (13 g.). The substance crystallises from toluene in pale green, microscopic needles, sintering at 163° and melting at 170° (Found : C, 55·3; H, 4·7. $C_{22}H_{22}O_8Cu$ requires C, 55·3; H, 4·6%). The free enol was obtained in the usual manner by means of dilute sulphuric acid in presence of ether, but could not be crystallised. It develops a purplish-brown coloration on the addition of ferric chloride to an alcoholic solution.

Pelargonidin Chloride 3 : 4′-*Dimethyl Ether*.—Through a solution of the hydroxymethylene derivative (1·2 g.) described in the last section and phloroglucinol (0·73 g.) in ether (20 c.c.), hydrogen chloride was led for 1 hour. The dark crimson crystals (0·6 g.) were crystallised by solution in hot very dilute hydrochloric acid which was brought up to 5% after filtration (Found, in material dried in a vacuum : C, 58·0, 58·0; H, 5·0, 5·0. $C_{17}H_{15}O_5Cl,H_2O$ requires C, 57·9; H, 4·8%). The reactions of this product were identical with those of a specimen of dimethylpelargonidin chloride obtained from 2 : 4 : 6-triacetoxybenzaldehyde as described by Pratt and Robinson (*loc. cit.*), but the latter was anhydrous. We therefore crystallised the specimen (P. and R.) under the conditions employed above, but nevertheless got the same results as before (Found : C, 60·7; H, 4·7. Calc. for $C_{17}H_{15}O_5Cl$: C, 61·0; H, 4·5%). The *perchlorates* derived from both specimens were obtained by crystallisation from acetic acid in dark crimson, plank-shaped crystals of identical appearance. The hydrated-chloride specimen melted with decomposition at 221°, and that derived from the anhydrous chloride (P. and R.), and also an intimate mixture of the two, at 220°.

Pelargonidin Chloride.—Dimethylpelargonidin chloride (2 g., prepared as described above), phenol (12 g.), and hydriodic acid (50 c.c.; *d* 1·7) were heated together at 150° for 30 minutes. The crystals which separated on cooling were collected, washed with ether, and the iodide was converted to chloride by means of precipit-

ated silver chloride and a little hydrochloric acid in hot methyl-alcoholic solution (35 c.c.). The filtered solution was mixed with 6% hydrochloric acid (50 c.c.), and 0·7 g. crystallised on standing (Found, in material dried in a vacuum: C, 55·9, 56·0; H, 4·2, 4·2, $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·5; H, 4·0%). This material exhibited the chief reactions of pelargonidin, but was not pure and the crystals did not possess a sufficient resemblance to those of pelargonidin chloride to render identification certain. A small specimen of undoubted pelargonidin chloride was, however, obtained as follows. The crude chloride was converted into iodide by crystallisation from a mixture of hydriodic acid and phenol and, after transformation of the iodide to chloride in the usual manner, 7% aqueous hydrochloric acid was added to the alcoholic solution, and the latter evaporated in a vacuum. The first fraction of nearly square-cut prisms was not quite homogeneous and was recrystallised in the same way. Twinned prisms were obtained and these were thrice recrystallised from very dilute hydrochloric acid solution by the addition of concentrated acid. At first, fern-like masses and then clusters of flat prisms were obtained. Recrystallisation by the evaporation of an alcoholic solution to which 7% hydrochloric acid had been added gave thick prisms which had the characteristic shape of those described by Willstätter and Burdick (*Annalen*, 1916, **412**, 163) and of which microphotographs were reproduced. The specimen exhibited the solubility relations, reactions, and absorption spectrum in alcoholic solution of pelargonidin chloride, but this was also true of specimens which nevertheless did not crystallise in the form regarded as typical of the pure anthocyanidin.

The authors wish to thank the Chemical Society for a grant which covered a part of the cost of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, March 17th*, 1925.]

CLXV.—*Nitration of the Carbonate and Ethyl Carbonate of* m-*Hydroxybenzaldehyde.*

By FREDERICK ALFRED MASON.

THE nitration of *m*-hydroxybenzaldehyde has been frequently investigated (Farbwerke vorm. Meister, Lucius, & Brüning, D.R.-PP. 18016, 20116; Tiemann and Ludwig, *Ber.*, 1882, **15**, 2044, 2052, 3052; Schnell, *Ber.*, 1884, **17**, 1381; Ulrich, *Ber.*, 1885, **18**, 2571; Tiemann, *Ber.*, 1889, **22**, 2339, 2347; Pschorr

and Seidel, *Ber.*, 1901, **34**, 4000; Friedländer and Schenck, *Ber.*, 1914, **47**, 3040; Henry and Sharp, J., 1924, **125**, 1049), and Friedländer and Schenck have shown that from 100 g. of the aldehyde 40 g., 36 g., and 12 g. of the 6-, 4-, and 2-nitro-derivatives, respectively, are produced.

In view of the orienting effect of the carbonate group, shown, for instance, in the case of *p*-tolyl carbonate, which nitrates almost exclusively in the meta-position to the carbonate group, whilst *p*-cresol itself nitrates chiefly ortho to the hydroxyl group, the nitration of the carbonate and ethyl carbonate of *m*-hydroxybenzaldehyde has been examined in order to ascertain the position of the nitro-group in the products.

In both cases nitration was effected chiefly in position 6, the yield of 6-nitro-3-hydroxybenzaldehyde isolated after hydrolysis being about 83% of the theoretical in the case of the carbonate, the product crystallising in an almost pure condition when the solution of the hydrolysed carbonate was acidified. This process therefore offers an excellent method for the preparation of the 6-nitro-compound, as the older method of direct nitration of *m*-hydroxybenzaldehyde involves a laborious process of separation by fractional crystallisation.

Experimental.

[In part, with H. Jenkinson.]

m-*Aldehydophenyl Carbonate.*—The direct addition of carbonyl chloride to a solution of *m*-hydroxybenzaldehyde in the calculated quantity of aqueous sodium hydroxide gave a mixture of about equal parts of the carbonate and free hydroxybenzaldehyde.

To a solution of *m*-hydroxybenzaldehyde (122 g.) and sodium hydroxide (40 g.) in water (1200 c.c.), saturated sodium carbonate solution (500 c.c.) was added and the whole saturated with sodium chloride, any precipitate formed being ignored. The deep red solution was diluted with crushed ice (500 g.), transferred to two 1½-litre flasks connected in series, and carbonyl chloride was passed in slowly so that about one bubble escaped from the exit tube in 2 seconds. After 1 hour, the two flasks were interchanged and the current of carbonyl chloride was continued for ½ hour; at this stage, the solutions were almost colourless and pasty. The gas was then passed in rather more rapidly and the flasks were shaken; after a few minutes, frothing commenced, due to evolution of carbon dioxide; the gas was passed for a further 20—30 minutes and then stopped. The temperature usually remained well below 40°, the whole operation occupying about 2 hours. The white precipitate

was practically freed from sodium chloride by washing with water, ground up with 100 c.c. of glacial acetic acid, washed with water and with alcohol, dried, and crystallised from glacial acetic acid; m. p. 132—134°, yield about 122 g. (90%). The carbonate is sparingly soluble in most organic solvents and is readily hydrolysed by aqueous alkalis.

Nitration.—The finely powdered carbonate (54 g., free from sodium chloride) was added slowly to 98% sulphuric acid (600 c.c.) at 0° with vigorous stirring and cooling, in a freezing mixture. A mixture of 90% nitric acid (20 c.c.) and concentrated sulphuric acid (100 c.c.) was run in slowly during ½—1 hour, the temperature being kept at 0—5°; after being stirred for ¾ hour, the brownish-black liquid was poured on to crushed ice, when 4-nitro-3-aldehydophenyl carbonate separated as a pale buff-coloured, granular solid. After 24 hours, the product was collected, washed with water until free from acid, then with alcohol, dried on the water-bath (yield about 70 g.; 97%), and crystallised from glacial acetic acid. The carbonate melts at 194—198° (decomp.), softening somewhat below this temperature (Friedländer and Schenck, *loc. cit.*, p. 3044, give 202°). It is insoluble in hot alcohol, tetrachloroethane, acetone, or benzene, but is readily soluble in hot glacial acetic acid or nitrobenzene (in the latter case with considerable decomposition). It discolours on exposure to light.*

Hydrolysis of the Nitro-carbonate.—The nitro-carbonate (35 g.) was added in quantities of about 5 g. to 200 c.c. of 4% sodium hydroxide, heated on a water-bath, a small extra amount of alkali being added finally if necessary. The solution was neutralised with acetic acid and cooled in a freezing mixture for a few hours. The dark brown, crystalline product (yield about 31 g.; 95%) was crystallised several times from 10% aqueous alcohol; it then melted at 167°. 6-Nitro-3-hydroxybenzaldehyde is slightly soluble in water or ether, soluble in acetone, glacial acetic acid, nitrobenzene, or pyridine, very soluble in methyl or ethyl alcohol, and insoluble in chloroform, benzene, or toluene. It has very marked sternutatory properties, the presence of a few mg. in the atmosphere causing violent sneezing. The identity of the substance was proved by its melting point, by the sensitiveness to light characteristic of *o*-nitrobenzaldehydes, and by its conversion into the yellow methyl ether, m. p. 83—84°, which, on treatment with acetone and dilute alkali, gave the corresponding dimethoxyindigotin.

m-*Aldehydophenyl Ethyl Carbonate.*—To a cooled, filtered solu-

* On several occasions, under the same experimental conditions, the nitro-product became tarry during filtration, but it still gave a nearly normal yield on hydrolysis.

tion of *m*-hydroxybenzaldehyde (122 g.) and sodium hydroxide (40 g.) in water (900 c.c.), ethyl chlorocarbonate (108·5 g. = 95 c.c.) was added with stirring during ¾ hour, the temperature rising to 30°. The mixture was stirred for ½ hour, and the oily product isolated by means of ether; it distilled almost entirely at 165–167°/20 mm. (yield 184 g.; 95%) as a viscous, colourless or pale yellow oil, *d* 1·42, which was insoluble in water.

The ethyl carbonate is quite stable in an ordinary stoppered bottle. It boils under normal pressure at 289—292° with slight decomposition and does not crystallise, even in a freezing mixture. It is slowly hydrolysed by warm aqueous alkalis, but is more resistant than the carbonate.

Nitration.—The ethyl carbonate (48·6 g. = 34·2 c.c.) was dropped into a mixture of 3% oleum (200 c.c.), 96% sulphuric acid (200 c.c.), and 90% nitric acid (20 c.c.) during 2 hours with good stirring, the temperature being kept below 5°. After 2 hours' stirring, the product was poured on to ice, and the finely crystalline precipitate was well washed with water, pressed, and dried on the water-bath (yield 45·8 g.; 96%).

The product appeared to be a mixture, which has not been separated, but after two crystallisations from benzene–light petroleum (b. p. 60—80°) about half of it was obtained in nearly colourless crystals, m. p. 63—65°. Hence the crude nitration product seems to consist of at least 50% of this (4-nitro) isomeride.

Hydrolysis of 4-Nitro-3-aldehydophenyl Ethyl Carbonate.—The crude nitration product (13 g.) was suspended in water (50 c.c.), the calculated quantity of dilute sodium hydroxide solution added gradually, and the mixture boiled for a short time until the oil had disappeared. The solution was cooled, acidified with glacial acetic acid (7 c.c.), and cooled in ice. The yellow, crystalline precipitate was identified as 6-nitro-3-hydroxybenzaldehyde (yield 3·4 g.; 41%).

Note on some Derivatives of 6-Nitro-3-hydroxybenzaldehyde.

As the simple derivatives are not very fully described in the literature, some experiments were done upon their methods of preparation.

The methyl ether, m. p. 83°, was obtained in 90% yield by stirring methyl sulphate (126 g.) in a solution of 6-nitro-3-hydroxybenzaldehyde (83·5 g.) and sodium hydroxide (30 g.) in water (350 c.c.) at 40°, more alkali being occasionally added until a permanent alkaline reaction was obtained; 6-nitro-3-methoxybenzaldehyde was precipitated in a crystalline condition.

The monoacetyl derivative, m. p. 74° (Friedländer and Schenck

loc. cit.), was obtained by acetylation with acetyl chloride and pyridine; and a *triacetyl* derivative, m. p. 120°, by the action of acetic anhydride and a drop of sulphuric acid at 40—50° and dilution with water.

The benzoyl derivative, m. p. 104—105°, was obtained in quantitative yield by means of pyridine and benzoyl chloride.

The *phenylhydrazone*, m. p. 185—195° (decomp.), separated in red crystals on mixing the aldehyde and phenylhydrazine in acetic acid solution. The sodium salt forms deep red crystals melting above 270°.

The *oxime* forms pale yellow needles, m. p. 179—180°; it is very easily soluble in alcohol and forms an orange-red sodium salt.

The *semicarbazone*, prepared in the usual way, forms pale yellow crystals, decomp. 245—260°. It is soluble in alcohol and forms an orange sodium salt.

The author's thanks are due to Professor W. H. Perkin, F.R.S., and to the British Dyestuffs Corporation, Ltd., for permission to publish the results of the investigation.

DYSON PERRINS LABORATORY,
OXFORD. [*Received, February 13th*, 1925.]

CLXVI.—*The Tautomerism of Dyads. Part III. The Effect of the Triple Linking on the Reactivity of Neighbouring Atoms.*

By EDITH HILDA INGOLD.

THE chemistry of substances containing an acetylenic linking has, on the whole, been investigated more from the point of view of the reactions of the unsaturated centre itself, than of its effect on the other atoms in the molecule. Effects of the latter kind are, nevertheless, remarkable, and to direct attention to them is the purpose of this paper.

There is a profound difference between ethylenic and acetylenic bonds, for a hydrogen atom, when attached to an ethylenic carbon, is firmly bound, but when attached to an acetylenic carbon, is easily replaceable by metals, and, at any rate in certain of the simpler cases, possesses tautomeric mobility (E. H. Ingold, J., 1924, **125**, 1528). Very probably this phenomenon is not confined to the simpler cases; for whilst potentially mobile acetylene acids of the type $HC{:}C{\cdot}[CH_2]_n{\cdot}CO_2H$ are comparatively stable, static acids of the type $CO_2H{\cdot}C{:}C{\cdot}[CH_2]_n{\cdot}CH_3$ show a strong tendency to acquire an

acetylenic hydrogen * atom by loss of carbon dioxide. This behaviour is analogous to that of blocked triad systems, and suggests that the tendency to form a mobile structure may, in both cases, determine the extrusion of a group. The fact that acetylenedicarboxylic acid, on gentle heating with water, loses only one molecule of carbon dioxide further supports this view, for both carboxyl groups, being similarly situated with reference to the triple bond, should be eliminated if the group $\cdot C{:}C\cdot CO_2H$ possessed intrinsic instability.

The anomalous effect of the acetylenic linking is particularly marked in the case of the halogen derivatives of acetylene (E. H. Ingold, *loc. cit.*). Thus the normal order of reducibility of halogens in corresponding structures, *viz.*, I > Br > Cl, is inverted in the case of the dihalogenacetylenes, di-iodoacetylene being the most stable, and dichloroacetylene the least.

Again, Feist's failure (see also the experimental portion of this paper) to obtain simple condensation products between ethyl tetrolate and ethyl oxalate (*Annalen*, 1906, **345**, 108) forms a striking contrast with the condensation of ethyl crotonate with ethyl oxalate (Lapworth, J., 1901, **79**, 1276), and appears to show that there is a marked difference in the power of ethylenic and acetylenic linkings to transmit an activating effect from an α- to a γ-carbon atom.

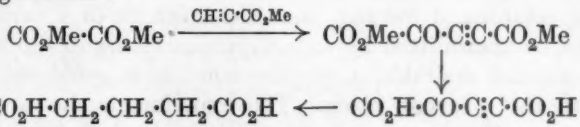
In view of the close connexion between triad tautomerism and γ-activation (Lapworth, *loc. cit.*), it was considered of interest to determine whether the dyad changes associated with the acetylenic linking would have their counterpart in the production of β-activation, that is, whether the influence of a carbethoxyl group can be transmitted through an acetylenic linking to the β-carbon atom. The experiments now described show that this can occur, and that the β-hydrogen atom in propiolic ester is so reactive that it not only undergoes Claisen condensations, with loss of alcohol, with compounds such as ethyl oxalate, but also undergoes the Michael addition reaction with, for example, ethyl fumarate. As the acetylenic hydrogen atom in a hydrocarbon shows a certain amount of reactivity, for instance, towards aldehydes † (Nef, *Annalen*, 1899, **308**, 281; Moureu and collaborators, *Bull. Soc. chim.*, 1902, **27**, 361 *et seq.*), it was thought that the condensations of propiolic esters might be due solely to the grouping HC:C. Experiments showed, however, that amylacetylene does not condense with ethyl oxalate under conditions similar to those used for the corresponding condensations with propiolic esters. It follows that the

* The term is used in this paper for hydrogen in the combination $\cdot C{:}CH$.

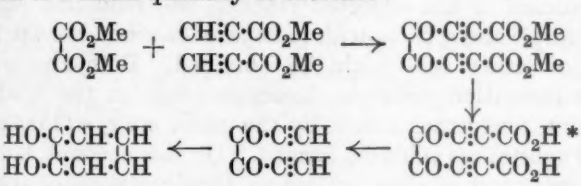
† Formic esters also react in certain cases, and may be included under the term "aldehyde."

carbethoxyl group in propiolic esters definitely enhances the reactivity of the acetylenic hydrogen atom. The phenyl group also appears to enhance the effect of the triple bond to a small extent, for phenylacetylene combines with certain substances which will not unite with amylacetylene (Moureu and Delange, *loc. cit.*, p. 378).

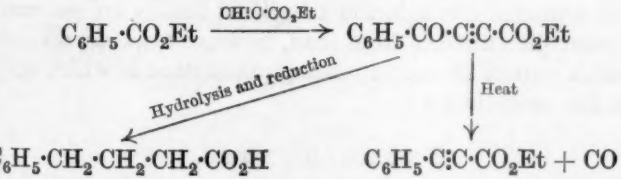
Owing to the tendency of triple-bonded structures to add on sodium ethoxide, the Claisen reactions between methyl and ethyl propiolate on the one hand, and oxalic and benzoic esters on the other, were carried out in the absence of alcohol. The products, however, showed marked instability, and their tendency to pass into other substances during isolation was such that, in the later experiments, the mixture of acids obtained after hydrolysis of the condensation product was completely reduced to the corresponding fully saturated compounds. When, for example, methyl propiolate and methyl oxalate were employed, the principal reduction product was glutaric acid, the formation of which must be represented by the following scheme :



Evidence that methyl oxalate had also combined to some extent with two molecules of methyl propiolate was provided by the isolation of a small quantity of catechol :

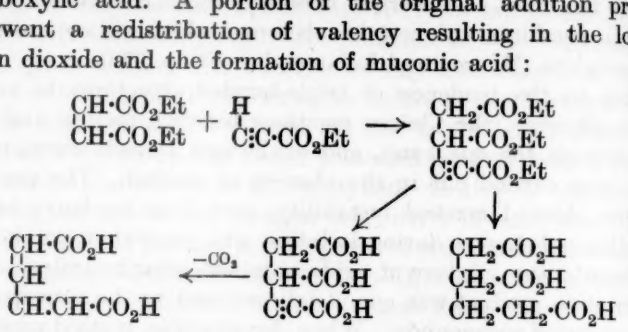


Similar results were obtained in the condensation of ethyl propiolate with ethyl benzoate, the product, after hydrolysis and complete reduction, yielding γ-phenylbutyric acid. If, before hydrolysis, the crude product was distilled, ethyl phenylpropiolate was produced, evidently from the keto-ester by loss of carbon monoxide :



* Examples of loss of carbon dioxide from analogous acetylenic acids are given on p. 1199.

Ethyl propiolate combined readily with ethyl fumarate, and the product, after hydrolysis and reduction, yielded *n*-butane-αβγ-tricarboxylic acid. A portion of the original addition product underwent a redistribution of valency resulting in the loss of carbon dioxide and the formation of muconic acid:



This loss of carbon dioxide during intramolecular rearrangement is reminiscent of Baeyer's experiences with the dihydroterephthalic acids (*Annalen*, 1892, **269**, 170).

Having established the fact that the influence of a carbethoxyl group can be transmitted by an acetylenic linking to the β-carbon atom, it seemed desirable to enquire whether it could not also be carried to the γ-carbon atom. The experiments, however, were inconclusive. Feist's experiments on the condensation of ethyl oxalate with ethyl tetrolate (*loc. cit.*) were repeated, and the reduction method was applied to the products. If the condensation were to proceed in the expected manner, the reduction products should be adipic and sebacic acids (compare the schemes on p. 1201). No trace of either acid could be obtained. Both the possible original condensation products, however, offer, at the methylene groups, points for further attack by the oxalic ester, so that a large number of substances could be formed. On this account, failure to recognise any product does not prove that reactions of the type indicated do not occur.

From the examples given, namely, (1) the dyad migration of hydrogen in acetylenes, (2) the inversion of the usual order of reactivities of chlorine, bromine, and iodine in the halogen acetylenes, (3) β-activation in acetylene esters, it is clear that the effects induced by, or transmitted through, the acetylenic linking are governed by special principles distinct from (and, in some respects, opposite to) those which control the corresponding phenomena in which ethylenic linkings are concerned.

EXPERIMENTAL.

Preparation of Propiolic Acid.—Chlorofumaryl chloride (Perkin, J., 1888, **53**, 695) (100 g.) was dropped very slowly, with continual

shaking, into 3*N*-ethyl-alcoholic potassium hydroxide (1300 c.c.) cooled in a freezing mixture. The mixture of potassium chloride and potassium acetylenedicarboxylate obtained (about 210 g.) was dissolved in water (about 450 c.c.), treated with dilute sulphuric acid (60 g. of a mixture of 700 c.c. of water with 300 c.c. of sulphuric acid), and the precipitated potassium hydrogen acetylenedicarboxylate (90 g.) heated with water (160 c.c.) for 1 hour on the steam-bath. The filtered solution was acidified with sulphuric acid (62 g. of the above strength), extracted thrice with ether (1 litre each time) dried with sodium sulphate, and distilled under diminished pressure (yield about 100 g. from 680 g. of chlorofumaryl chloride). This process has the advantage over Perkin and Simonsen's (J., 1907, **91**, 843) in that the preparation of dibromosuccinic acid in quantity is avoided.

Methyl Propiolate.—Sulphuric acid (2·85 g.) was added, with cooling, to propiolic acid (9·5 g.) dissolved in pure methyl alcohol (20 c.c.). After being kept for 2 days at the ordinary temperature, the mixture was poured into iced water and extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate solution to remove unchanged propiolic acid (which was recovered), dried with calcium chloride, and distilled through an efficient fractionating column, 6·3 g. of *methyl propiolate* being obtained as a colourless, lachrymatory liquid, b. p. 102°/742 mm. (Found: C, 57·0, H, 5·0. $C_4H_4O_2$ requires C, 57·15; H, 4·8%).

Ethyl propiolate was prepared by Perkin and Simonsen's method (*loc. cit.*). Yield 5·5 g. from 9·5 g. of propiolic acid.

Action of Alcoholic Sodium Ethoxide on Ethyl Propiolate: Formation of Ethyl ββ-Diethoxypropionate.—The ester (4·9 g.), diluted with ether, was added slowly to alcoholic sodium ethoxide (from 1·15 g. of sodium and 15 g. of alcohol), also diluted with ether, and the mixture was poured into water and extracted with ether. The *ethyl ββ-diethoxypropionate* recovered from the ethereal extract boiled at 206°/754 mm. (Found: C, 56·4; H, 9·4. $C_9H_{18}O_4$ requires C, 56·8; H, 9·5%).

Claisen Reactions with Propiolic Esters.

Methyl Propiolate and Methyl Oxalate.—In the preliminary experiments, the products of condensation, which was carried out as described below, were separated into neutral and acid portions in the usual way, with ether and sodium carbonate. Both fractions gave a deep yellow colour with sodium hydroxide, and an intense red colour with ferric chloride; but by hydrolysis only oxalic acid could be obtained, and all attempts to isolate the methyl αγ-diketoglutarate (from $CO_2Me{\cdot}CO{\cdot}C{\vdots}C{\cdot}CO_2Me$), probably present in the

neutral fraction, were frustrated by the extensive decomposition which ensued on distillation. The following method of experiment was therefore followed. Methyl propiolate (5 g.) was added to finely-divided sodium (1·37 g.) mixed with a solution of methyl oxalate (7·04 g.) in pure dry ether (110 c.c.). The mixture was heated on the steam-bath for 5 hours, when much darkening took place, and, after keeping over-night, the undissolved sodium was decomposed by the addition of ice. The solution was acidified, extracted with ether, and the extract separated into neutral, acid, and quasi-acid * fractions.

The neutral fraction was heated under diminished pressure on the steam-bath to remove unchanged esters, and the dark brown residue, after hydrolysis with cold methyl-alcoholic potassium hydroxide, was poured into water, and most of the methyl alcohol removed by a stream of air at the ordinary temperature. The product was reduced by Clemmensen's method, amalgamated zinc being added to the strongly acidified solution, which was kept for 1 day at the ordinary temperature, and 1 day on the steam-bath, when it became almost colourless. Ether extracted from the cooled product a mixture of solid acids, which were dissolved in water (100 c.c.), neutralised with ammonia, and treated with calcium chloride, when a precipitate of calcium oxalate was produced. The filtrate was evaporated to small bulk (10 c.c.), and treated with barium chloride, when a very small precipitate of barium succinate was produced. (For the succinic acid, m. p. 184°, obtained from this precipitate, found: *M*, 117. Calc., *M*, 118.) After removal of the barium succinate, the filtrate was evaporated, acidified, and extracted with ether, which removed glutaric acid (0·8 g.), identified by m. p. 94°, mixed m. p., and analysis (Found: C, 45·3; H, 5·9. Calc., C, 45·5; H, 6·0%).

A small amount of oxalic acid was separated from the acid fraction, and the oily residue was mixed with the quasi-acid fraction, hydrolysed, reduced by Clemmensen's method, and the products extracted, as above described. After the ether had been evaporated and the dark brown oily product kept in a desiccator, crystals separated, which, on crystallisation from benzene, yielded prisms, m. p. 105°, which were identified as catechol by the colour reaction with ferric chloride, a mixed melting-point determination, and analysis (Found: C, 65·6; H, 5·3. Calc., C, 65·5; H, 5·45%). From the insoluble portion, which contained zinc, oxalic acid was obtained by dissolving in hydrochloric acid, and again extracting with ether.

* This term is used for fractions soluble in sodium hydroxide, but not in sodium carbonate.

Ethyl Propiolate and Ethyl Benzoate.—In the preliminary experiments ethyl benzoate (4·6 g.) was condensed with ethyl propiolate (3 g.), and the products were separated into neutral and acid fractions as described in the previous experiments. The reaction was more vigorous in this case, and a considerable quantity of tar was formed. The neutral fraction was distilled under diminished pressure, when ethyl benzoate (3·6 g.) was recovered. Decomposition then occurred, but a few drops of a high-boiling oil were collected, and identified as ethyl phenylpropiolate by the fact that on hydrolysis (with concentrated aqueous potassium hydroxide) phenylpropiolic acid was obtained, m. p. and mixed m. p. 137° (Found : C, 73·9; H, 4·1. Calc., C, 74·0; H, 4·1%).

The acid fraction yielded a small amount of a brown oil giving a red colour with ferric chloride, and probably containing the diketonic acid (compare p. 1203) $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, but no solid product could be isolated.

In the final experiments, the neutral fraction was distilled at 1 mm. from a bath at 118°, when a considerable amount of unchanged ethyl benzoate passed over. The residue was hydrolysed and reduced as in the experiments with ethyl oxalate, when a liquid acid was isolated, which solidified on seeding with γ-phenylbutyric acid, and was identified as this acid by a melting point (47—48°) and mixed melting point determination.

The acid and quasi-acid fractions were resinous, and yielded only a small amount of benzoic acid on sublimation.

Michael Reactions with Propiolic Esters.

Ethyl Propiolate and Ethyl Fumarate.—These reactions were carried out in ethereal solution in the presence of finely divided sodium as previously described, and, as in the above experiments, much darkening occurred. In the preliminary attempts to effect these reactions, water was added to the condensation product, and the neutral portion isolated with ether. Owing, however, to the extensive decomposition on distillation, it was found impossible to isolate any pure product. In the subsequent experiments, therefore, the undistilled neutral product (from 8·78 g. of ethyl fumarate, 5 g. of ethyl propiolate, and 1·17 g. of " molecular " sodium) was hydrolysed with cold methyl-alcoholic potassium hydroxide, and the acids so obtained were reduced by Clemmensen's method. The solid acids obtained after extraction and vacuum desiccation were rubbed with a little ether. The portion soluble in ether was identified as succinic acid by a melting point and mixed melting-point determination. The insoluble portion, after crystallisation first from ethyl acetate and then from benzene and acetone, melted

at 118—120°, and was identified as butane-αβδ-tricarboxylic acid by a mixed melting-point determination and by analysis (Found: C, 44·0; H, 5·2; *M*, 191. Calc., C, 44·2; H, 5·25%; *M*, 190).*

The quasi-acid fraction yielded only a trace of resin, but the acid fraction partly solidified on keeping in a vacuum desiccator. The acid melted at about 300°, but as the small quantity available was contaminated by resinous material in a way that made crystallisation from water impossible, its identification as muconic acid was accomplished by conversion (by means of phosphorus pentachloride and alcohol) to ethyl muconate, which was identified by a melting-point (62—64°) and mixed melting-point determination.

Attempted Condensation of Amylacetylene with Ethyl Oxalate.

The amylacetylene (3·2 g.), prepared from heptaldehyde through the dichloride by Limprecht's method (*Annalen*, 1857, **103**, 84), mixed with ethyl oxalate (4·8 g.) was added to finely divided sodium (0·77 g.) in pure, dry ether. When the sodium had disappeared, the product was worked up in the usual way, but only amylacetylene and oxalic acid could be obtained.

Attempted Condensation of Ethyl Tetrolate and Ethyl Oxalate.

Ethyl tetrolate (5 g.), prepared by Stolz's method (Beilstein, "Organische Chemie," II, p. 480), was added to an ethereal solution of ethyl oxalate (6·5 g.) containing finely divided sodium (1 g.) in suspension. The mixture was boiled until the precipitate first formed (compare Feist, *loc. cit.*) disappeared. Ice was added, the solution acidified and extracted with ether, and the extract separated into neutral, quasi-acid, and acid fractions, all of which were dark brown oils. The neutral and quasi-acid fractions were hydrolysed with cold methyl-alcoholic potassium hydroxide, and then all three fractions were reduced as before. The reduction products, however, were largely resinous, and nothing but oxalic acid could be isolated in a pure condition.

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THE UNIVERSITY, LEEDS. [*Received, April 1st*, 1925.]

* This acid "clings" to the solvents employed for crystallisation with great tenacity, and must be dried at 100° before satisfactory analyses can be obtained.